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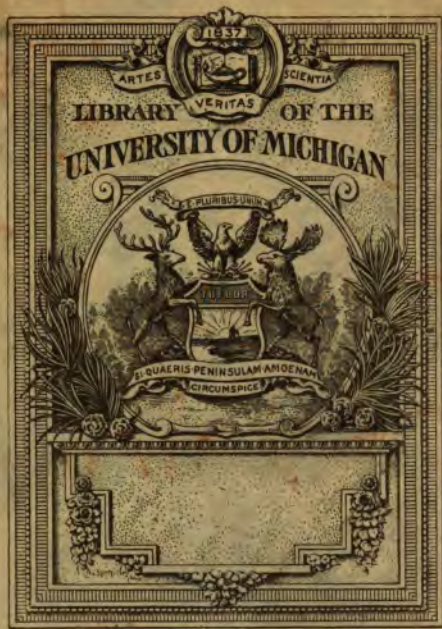
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**ELEMENTS**  
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**CHEMISTRY.**

**IN TWO VOLUMES.**

**BY**



**JOHN MURRAY, F.R.S.E.**

**LECTURER ON CHEMISTRY AND ON MATERIA MEDICA AND PHARMACY,  
EDINBURGH.**

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**THE THIRD EDITION.**

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**VOLUME FIRST.**

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## NOTICE.

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**I**n this Third Edition, I have been careful to insert all the recent discoveries in Chemical Science, and by employing a fuller page, I have been enabled to do so, without adding to the size of the volumes. The plan of the Work is still entirely Elementary,—being designed to present such a view of Chemistry as shall convey a just knowledge of its leading principles and more important facts, without including the discussion of controverted opinions, or the statement of those minute details which have with propriety a place in a Systematic Treatise.

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# INTRODUCTION.

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GENERAL VIEW OF THE NATURE, OBJECTS, AND APPLICATIONS OF CHEMISTRY. HISTORICAL SKETCH OF ITS ORIGIN AND PROGRESS. PRINCIPLES OF CHEMICAL ARRANGEMENT.

**T**HE minute particles of matter are not, as the external aspect of bodies would lead us to conclude, in a state of rest. They are acted on by certain powers, which preserve them in a state of motion, or at least induce that state, so as to give rise to an extensive series of changes, which form an established part of the economy of nature. Similar changes are induced by artificial arrangements, which either cause these powers to operate where they would otherwise be quiescent, or modify their operation where they are naturally exerted.

The phenomena arising from these actions, and the laws they observe, are the subjects of investigation in the Science of Chemistry.

The powers by the operation of which they are produced, are that species of attraction which is exerted exclusively between the minute particles of matter, and certain forces of repulsion by which this attraction is counteracted or modified.

Besides the general tendency which bodies even in the largest masses, and at the greatest distances, have to approach until they come into apparent contact, the operation of which gives rise to those sensible motions which constitute so important a part of the system of the universe, — there exists a similar tendency in the ultimate particles of matter to approach and enter into intimate union. When this attractive force unites particles of a similar kind, it forms masses possessed of the same essential properties, and distinguished according to their state of aggregation, by peculiarities of structure, or physical form. When it unites those of a dissimilar nature, it forms new substances, deriving the specific properties which belong to them from their chemical constitution.

The principal repulsive force by which this attraction is counteracted, is the power of Heat, or what in modern chemistry is named Caloric. Its immediate operation is to place the particles of matter at greater distances from each other; it thus changes the forms and qualities of bodies, and subverts the combinations which attraction has produced. Light, from its relation to heat, is frequently productive of similar effects; independent of peculiar chemical agencies it exerts. And Electricity, under that modification in particular which constitutes Galvanism, is still more powerful in its action, counteracting attractions which heat alone cannot overcome.

In all these cases, the immediate effect is the motion of the particles with regard to each other; the ultimate re-



sults are changes of constitution and form. Bodies are combined together, or are separated from states of combination in which they exist; and Chemistry, the department of natural knowledge under which these actions are classed, may be defined, The science which investigates the combinations of matter, and the agencies of those general forces whence these combinations are established and subverted.

This character of chemical action—that it is exerted between the particles of bodies, forms the leading distinction between it, and those actions, the investigation of which belongs to the other branches of natural philosophy. Connected with this are other peculiarities by which it is farther defined.

The properties of bodies, depending in a great measure on the peculiar arrangements of their particles, a change in the latter must necessarily be accompanied with a greater or less alteration in the former. Hence chemical action gives rise to a change of properties in the bodies between which it is exerted, and is indeed the great source from which the secondary qualities of bodies are derived. From any other species of physical action this result is not obtained, the effect being merely that of modifying motion in masses of sensible size.

Chemical action being exerted between the particles of matter at distances altogether imperceptible, admits of no exact measurement, as to its direction or force. The principles of chemistry, therefore, cannot be established on mathematical evidence, as the principles of the other physical sciences can, in which the objects of investigation are changes arising from sensible motion, which admits of precise determination.

It is from chemical action that the greater number of natural substances derive their origin. The number of those that are simple, that is, of those which consist only of similar parts, is inconsiderable. By mutual combinations of these, an extensive series of compounds is produced: these compounds are farther capable of combining with each other; and thus, from a few ultimate elements, probably still unknown to us, all the existing varieties of matter are formed.

Actions so extensive and important must be connected with many of the established operations of nature, and must admit of numerous applications to purposes of utility in the various arts. Of these connections and applications of Chemistry, a full development, even under a general point of view, would be incompatible with the limits of this preliminary discourse; and a few examples may convey an idea of the extent of the science, and of the interest which its study is calculated to excite.

No view of adjustment in the economy of nature is more admirable than that which Chemistry traces with regard to the temperature of the globe, the sources of its variations, and the limits within which these are restrained. That degree of heat which is necessary to sustain the greater number of natural operations, is derived from the action of the solar rays on the surface of the earth; but from the mode in which this is communicated, it is necessarily unequal, or prevails in different degrees of intensity at different seasons, and at different regions of the earth; and did not certain arrangements exist, this inequality would continue progressive. These arrangements Chemistry unfolds: it has discovered that absorption of heat which attends the rarefaction of the atmosphere, the evaporation of water,

and the melting of ice, and that evolution of heat which accompanies the reverse changes, and has established the laws by which these are regulated. It has thus enabled us to trace the causes by which the extremes of climate and the transitions of seasons are moderated, and the temperature over the surface of the globe is preserved within comparatively a limited range.

Chemistry has still to investigate another adjustment in the economy of nature, the necessity for which the researches of this science have alone discovered. That air is indispensable to living beings, is sufficiently demonstrated by familiar facts; but that this air, in being breathed by animals, is rapidly deteriorated, and rendered at length unfit to sustain life, is established by the experiments of the Chemist; and it is only by these experiments that the change of composition from which this arises is made known. It is of course only from the successful prosecution of these researches that we can discover the natural operations by which it is counteracted, and the due purity of the atmosphere is preserved.

The spontaneous evaporation of water, its elevation in clouds, and its deposition in the form of dew, rain and snow, are dependant on chemical action. From the principles of this science, the laws which regulate these processes, so far as they are known, have been illustrated, and it is only from the extension and more strict application of these principles that their theory can be fully explained.

We observe the chemical agency of water in many other natural operations; in its action, for example, on the surface of the earth, the disintegration it occasions, and the ultimate formation of soil; and still more in the processes of animated existence, particularly in sustaining the growth

of plants, and affording or conveying to them the principles whence their products are formed.

By discovering to us, that the substances which belong to the Mineral Kingdom are compounds of certain elements, Chemistry demonstrates that their formation must have been the result of chemical combinations; and the application of its principles must afford the explanation of those arrangements, which the observations of the Geologist, skilfully generalized, have demonstrated to prevail in the structure of the solid parts of the globe. It will also ultimately give the only sure basis on which the *species* of minerals are established and arranged, by discovering the varieties of composition on which this depends.

We can trace the predominance of chemical action, not less in the processes of animated nature, though these, from their obscurity and complication, are more difficult of elucidation. In vegetation we discover a series of operations, in which the principles conveyed to the growing plant are brought into new combinations, so as to form its diversified products: some of the chemical agencies connected with it have been already successfully investigated; and in the progress of the science we may, without any undue confidence, predict its full development, as a result of chemical affinities, modified by the circumstances under which they are exerted. The chemical processes of the Animal System are still more complicated and more dependent on, or at least more intimately connected with, the peculiar laws of vitality; yet even in these, Chemistry has discovered a number of important truths; and the knowledge which it affords of the composition of the animal fluids and solids, not only aids the researches of the Physiologist, but often throws light on the inquiries of the Physician. The remedies produced by

chemical combinations are not less important in the practice of medicine.

With the processes of Art, Chemistry is not less strictly connected than with the operations of Nature ; nor would it be easy, in an Introductory Sketch, to do justice to its practical applications. The extraction of metals from their ores, the purifying, casting, and forging them, the production of metallic alloys, and of metallic pigments, are altogether dependant on this science : the manufactures of glass, of pottery and porcelain, consist merely of a series of chemical combinations : the processes of bleaching and of dyeing, of making starch, sugar, and vinegar, of fermenting and distilling, of tanning, of soap-making, and of preserving animal substances from putrefaction,—all of these, in their most minute details, are in the strictest sense of the term Chemical operations. It is from the skilful application of the principles of this science, rather than from the uncertain suggestions of chance or of random experiment, that the improvement of these arts is to be derived. The researches of Chemistry have already in this point of view led to important acquisitions. As it advances, its applications to purposes of utility will become more extensive, and more easily regulated ; and as it is unbounded in the objects of its investigations, we can assign no limits to the extent of these relations, nor foresee how far it may yet add to the power of man.

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THIS important department of Physical Science is altogether of modern origin. It had no place in the system of Ancient Philosophy : and though arts were practised from remote antiquity, the processes of which are dependent on

chemical actions, the relations of these were never discovered, their principles remained unknown, and no body of chemical knowledge existed to which a distinctive appellation could have been assigned.

Its origin is to be traced to a singular pursuit which commenced towards the decline of literature, and which continued for many ages to be followed with unabated ardour, —that of the art of transmutation, or of converting the baser metals into silver or gold. In the prosecution of these delusive researches, observations were necessarily made on the changes produced by the mutual chemical actions of bodies, and these gradually accumulated formed the base on which the science of Chemistry has been reared.

The date of the rise of Alchemy, as this pretended art of transmutation was named, is not exactly known. It has been traced to the fifth, the fourth, or even to the third century; but there is every reason to doubt of the authenticity of the authorities on which it has been referred to these early periods. Towards the close of the fifth century, some progress appears, however, to have been made in chemical, or rather alchemical investigations. Among the Arabians, who had received the science and literature of the Greek Empire, the study of alchemy was eagerly prosecuted; and transferred to Europe, it continued amid the darkness of the middle ages, and even to a later period, to delude and mislead those who endeavoured to penetrate the mysteries of nature. The ultimate failure of these laborious researches led to the suspicion of the soundness of the views from which they originated; and the real, though slow progress of experimental inquiry, enlightened by the more philosophical spirit of investigation which distinguished the sixteenth century, banished at length the follies and deceptions

of alchemy, and laid the foundation of chemical knowledge. The labours of the alchemists had not however been altogether fruitless; a number of important facts had been established; some of the most powerful chemical agents had been discovered; the instruments of the principal operations of Chemistry were invented, and the methods of conducting its processes were improved.

It is not the object of this sketch to follow with any minuteness the progress of Chemistry through its successive stages. It is sufficient to give it a more rapid glance. Kunckel, Homberg, Lemery, and Geoffroy, were its first eminent cultivators free from alchemical bias. Van Helmont had called the attention of Chemists to the aërial fluids so frequently disengaged in their experiments, and had even pointed out some of their properties and distinctions,—a subject prosecuted by Boyle, especially in so far as related to the action of atmospheric air, and by Mayow, with still more extensive and accurate views. Bacon fixed the limits of Chemistry, and assigned it its due rank in the scale of natural knowledge. Newton generalized its principal phenomena, by referring more distinctly the combinations and decompositions, which are the chief objects of its investigations, to the operation of that species of attraction exerted at insensible distances between the particles of matter. Boerhaave, besides investigating some particular subjects, more especially the effects of heat, presented the details of the science in a systematic form; and Margraaf, Rouelle, Macquer, and Bergman, enlarged its limits by the discovery of numerous facts, and by the elucidation of some of its principles. Beccher had sought to anticipate what is the final object of chemical investigations, and what will only be attained when these have reached perfection,—the determi-

nation of the elements from the combination of which all the existing varieties of matter are formed : and Stahl, adopting in part his views, but limiting his speculations to the operation of one principle, that to which the property of communicating inflammability was ascribed, framed an hypothesis so extensive in its chemical relations, as to have been regarded as a general system of the science, and so well constructed as to have commanded unlimited assent.

The process of Combustion is of primary importance in Chemistry, not only from the striking phenomena it displays, but from its affording in some measure a division of bodies founded on chemical relations, and from giving origin to some of the most important chemical agents. Changes analogous to those which occur in this process, are likewise produced by the operation of these agents ; and thus, whatever theory is framed of combustion itself, is farther extended, and is indeed capable of being more or less remotely connected with nearly the greater number of chemical phenomena. Stahl, to explain the phenomena of this important chemical operation, assumed the existence of a common principle, Phlogiston, as he named it, in inflammable bodies : its evolution, under the form of heat and light, constituted, he imagined, the process of burning : its disengagement, he considered as the cause of the change of properties, and particularly the loss of inflammability, which the body suffering combustion always sustains : its communication again to the burnt body restores therefore its original qualities ; and its transfer, in other cases of chemical action, gives rise to analogous effects.

This hypothesis connected a number of phenomena by a common principle, and apparently afforded a just explanation of them ; it was therefore generally received. Rest-



ing, however, on an imperfect knowledge of the facts which it generalized, the progress of the science discovered its imperfections, and established very different views.

Substances existing in the aërial form are, from their subtilty, apparently not easily subjected to the usual methods of chemical investigation ; and hence, although some of the facts connected with their formation and disengagement had attracted the attention of chemists, their chemical actions had never been clearly investigated, their distinctions established, nor the importance of their agency understood. Dr Black, by his discovery of the properties and combinations of one of these aërial substances, Fixed Air, or Carbonic Acid Gas, demonstrated the importance of these researches ; and after the publication of his experiments, the department of Pneumatic Chemistry was soon eagerly cultivated. By the discoveries of Cavendish, Priestley, Scheele and Berthollet, the existence of other aërial fluids, their properties, and chemical relations, were established : and Lavoisier, entering the same path of experiment, and availing himself of these discoveries, advanced speculations distinguished by their novelty and ingenuity, and which soon assumed the place of the hypothesis of Stahl. The existence of a peculiar aërial substance, Oxygen, as an element of atmospheric air, and the importance of this element in its chemical agencies, and particularly in sustaining the process of burning, had been established by the researches of Priestley and Scheele. These Lavoisier extended, and drew from them conclusions subversive of the established doctrine. The phenomena of combustion, and of all its analogous processes, which Stahl had ascribed to the evolution of phlogiston, he referred to the combination of oxygen. He traced the chemical agen-

cies of this principle, and framed a system seducing by its simplicity, resting apparently on a just induction, supported by experiments distinguished by precision, and which, after a short period of animated discussion, was universally received.

Since this period, Chemistry has continued to make a rapid progress. The theory of attraction has been more minutely and more successfully investigated; the knowledge of galvanism has led to the acquisition of a new and powerful instrument of chemical analysis, and every department of the science has been enriched by numerous insulated discoveries. Nor can any limits be placed to the extent of its investigations. Its analysis is indefinite: its termination will have been attained only when the real elements of bodies shall have been detected, and all their modifications traced: but how remote this may be from its present state, we cannot judge; nor can we, from our present knowledge, form any just conception of the stages of discovery through which it has to pass.

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THE last object in this introductory sketch is to state the principles on which the arrangements of Chemistry are formed.

The investigations of this science are directed to the actions which are exerted among the particles of matter, in consequence of which they pass into new arrangements and new states of combination, producing changes of constitution and properties. These actions arise from the operation of certain general forces on the particles of bodies, and different bodies are affected by these in modes peculiar to each. Hence the science obviously divides itself

into two great departments,—the first comprising the investigation of the general effects and laws of these forces; and the second considering their operation on individual substances. Under the former, are to be considered the doctrines of Attraction, and of its antagonist force Repulsion as produced by the operation of heat, light, and electricity; to the latter belongs the history of the chemical properties, and combinations of all known bodies.

The first of these divisions admits of little diversity of arrangement, nor is it of much importance in what order the subordinate parts belonging to it are placed. The second is more extensive and complicated; it presents therefore greater difficulties, and hence the numerous systems of chemical classification that have been proposed.

Two general methods are suggested by the nature of chemical investigations. Their leading object is to discover the composition of bodies, or, by analytic operations, to resolve them into the principles of which they are composed. The result of such researches is, that many bodies are decomposed, but others resist decomposition, or, even where it has been effected, substances are at length necessarily arrived at, beyond which the analysis cannot be carried. In the theory of Modern Chemistry, all such substances are regarded as simple; they are characterized by their most striking properties, and their combinations become subjects of farther investigation.

Now it is obvious, that in forming a system of chemical classification, we may, adhering to the synthetic mode, assume these simple substances as the basis of the arrangement, arrange them according to their chemical characters and relations, and place their compounds in a determinate order, according to their composition. Or we may adopt

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TABLE OF CLASSIFICATION.

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PART I.

OF THE GENERAL FORCES PRODUCTIVE OF  
CHEMICAL PHENOMENA.

---

OF ATTRACTION.

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OF THE ATTRACTION OF AGGREGATION.

— CHEMICAL ATTRACTION OR AFFINITY.

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OF REPULSION, AND THE POWERS  
BY WHICH IT IS PRODUCED.

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OF CALORIC.

— LIGHT.

— ELECTRICITY AND GALVANISM.

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**PART II.**

**OF THE CHEMICAL PROPERTIES AND RELATIONS  
OF INDIVIDUAL SUBSTANCES.**

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**OF ATMOSPHERIC AIR AND ITS PRINCIPLES.**

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**OF THE CONSTITUTION OF THE ATMOSPHERE.**

- OXYGEN.
  - NITROGEN.
  - ATMOSPHERIC AIR.
  - THE CHEMICAL AGENCY OF OXYGEN IN ITS PURE  
FORM, AND AS IT EXISTS IN ATMOSPHERIC AIR.
- 

**OF WATER AND ITS BASE.**

---

- OF HYDROGEN.**
- WATER.
- 

**OF ALKALIS AND THEIR BASES.**

---

- OF AMMONIA.**
- POTASSA AND ITS BASE.
  - SODA AND ITS BASE.
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## OF EARTHS AND THEIR BASES.

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### OF BARYTES AND ITS BASE.

— STRONTITES AND ITS BASE.

— LIME AND ITS BASE.

— ARGIL AND ITS BASE.

— MAGNESIA AND ITS BASE.

— SILEX AND ITS BASE.

— ZIRCON AND ITS BASE.

— GLUCINE AND ITS BASE.

— ITTRIA AND ITS BASE.

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## OF ACIDS AND THEIR BASES.

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### OF NITRIC ACID AND ITS BASE.

#### OF NITRIC ACID.

— NITROUS ACID.

— NITRIC OXIDE.

— NITROUS OXIDE.

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### OF SULPHURIC ACID AND ITS BASE.

#### OF SULPHUR.

— SULPHURIC ACID.

— SULPHUROUS ACID.

— SULPHURETTED HYDROGEN.

— SULPHURETTED AND HYDRO-SULPHU-

RETTEd ALKALIS AND EARTHS.

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OF CARBONIC ACID AND ITS BASE.  
OF CARBON.

- CARBONIC ACID.
- CARBONIC OXIDE.
- CARBURETTED, AND OXY-CARBURETTED  
HYDROGEN GASES.
- CARBURETTED SULPHUR.

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OF PHOSPHORIC ACID AND ITS BASE.  
OF PHOSPHORUS.

- PHOSPHORIC ACID.
- PHOSPHOROUS ACID.
- PHOSPHURETTED HYDROGEN.
- PHOSPHURETTED SULPHUR.

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OF BORACIC ACID AND ITS BASE.

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OF MURIATIC ACID AND ITS BASE.

- OF MURIATIC ACID.
- OXYMURIATIC ACID.
  - HYPER-OXYMURIATIC ACID.

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OF FLUORIC ACID AND ITS BASE

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**OF METALS.**

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**OF GOLD.**

— SILVER.  
— PLATINA.  
— IRIDIUM.  
— OSMIUM.  
— RHODIUM.  
— PALLADIUM.  
— QUICKSILVER.  
— COPPER.  
— IRON.  
— LEAD.  
— TIN.  
— ZINC.  
— NICKEL.

**OF COBALT.**

— MANGANESE.  
— ARSENIC.  
— BISMUTH.  
— ANTIMONY.  
— TELLURIUM.  
— CHROME.  
— MOLYBDENA.  
— TUNGSTEN.  
— TITANIUM.  
— URANIUM.  
— TANTALUM.  
— CERIUM.

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**OF THE NATIVE COMBINATIONS OF ACIDS, EARTHS,  
METALS AND INFLAMMABLES.  
MINERAL COMPOUNDS.**

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**OF SALINE MINERALS.**

— EARTHY MINERALS.  
— METALLIC MINERALS.  
— INFLAMMABLE MINERALS.  
— MINERAL WATERS.

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OF VEGETABLE COMPOUNDS.

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OF THE FORMATION OF VEGETABLE COMPOUNDS.

- THE CHEMICAL PROPERTIES AND RELATIONS OF VEGETABLE COMPOUNDS.
  - THE SPONTANEOUS CHEMICAL CHANGES AND DECOMPOSITIONS OF VEGETABLE COMPOUNDS.
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OF ANIMAL COMPOUNDS.

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OF THE FORMATION OF ANIMAL COMPOUNDS.

- THE CHEMICAL PROPERTIES AND RELATIONS OF ANIMAL COMPOUNDS.
  - THE SPONTANEOUS CHEMICAL CHANGES AND DECOMPOSITIONS OF ANIMAL COMPOUNDS.
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## PART I.

### OF THE GENERAL FORCES PRODUCTIVE OF CHEMICAL PHENOMENA.

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**T**HE powers which operate in producing chemical action, are that peculiar species of attraction which is exerted at insensible distances between the particles of matter, causing them to pass into new arrangements and new combinations, and certain forces of repulsion, by which this attraction is counteracted, and these arrangements and combinations are modified or subverted. In proceeding to the consideration of these general forces, the most natural method appears to be to place first the doctrines of attraction, and after these to consider the operation of its antagonist powers.

There is some difficulty, it must be admitted, in thus considering the general doctrines of Chemistry before its particular details; for as these doctrines are inferred by generalization from individual facts, the former cannot be thoroughly understood, or their evidence fully stated, while the latter are unknown. Hence some Chemists have proposed to reverse this order. But the difficulty is in reality one unavoidable in either mode of arrangement; for it is equally impossible to give the chemical history of a single

substance, without supposing a previous knowledge of the general phenomena and laws of chemical combination and chemical repulsion. Its history indeed as a chemical agent is confined to the attractive forces it exerts to other bodies, or to the changes it suffers either from such attractions exerted towards it, or from the operation upon it of those repulsive forces by which these attractions are modified. The laws of these general powers must therefore be previously known. In balancing the advantages and difficulties of these methods, the first, it appears to me, is entitled to the preference. It is possible to illustrate the general laws of chemical action by examples from substances familiarly known, or which, though unknown, are equally adapted to convey illustrations of abstract truths; and these laws being established, they may be developed and explained more minutely from the mutual actions of individual substances, while the history of these substances is given with more advantage, and can be rendered more complete, when the general doctrines have been previously delivered. There can scarcely be a heavier task, or one more calculated to damp the ardour of study, than to have to acquire the insulated facts of a science, unassisted by any knowledge of the principles which unfold their relations.

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**BOOK I.****OF ATTRACTION.**

**A**TTRACTION is a term employed in philosophical language to denote that power or force by which the masses or particles of matter have a tendency to approach to each other, and to enter into more or less intimate contact or union. Different species of attraction have been observed, which give rise to different phenomena, and operate, so far as can be traced, according to different laws.

The Attraction of Gravitation is exerted at sensible, and often at immense distances, and between masses of the greatest size: its force, according to the law demonstrated by Newton, being directly as the mass or quantity of matter, and inversely as the square of the distance. The Magnetic and Electric Attractions, though they give rise to peculiar classes of phenomena, so far coincide with the attraction of gravity, as to operate at sensible distances, and on masses of matter, and even, as has been attempted to be demonstrated, according to the same law.

Besides these, a species of attraction is exerted between the particles of matter, and at distances generally insensible. This force, when exerted between particles of a similar nature, is named the Attraction of Aggregation or Cohesion: when exerted between particles of different kinds, it is denominated Chemical Attraction, or Chemical Affi-

nity. Both are concerned in the production of chemical phenomena, and the latter is the force on which all the combinations of matter depend.

Both have been supposed to be ultimately the same power; the differences in the results of their operation being referred with probability to the difference of the particles on which they operate; aggregation uniting particles of a similar nature, and therefore producing, in each case, an aggregate possessed of similar properties; while chemical attraction, combining particles of different kinds, must give rise to products in which some modifications of properties will be the result. It has even been contended, that both are only modifications of that more general force which is exerted at sensible distances between the masses of matter; and the apparent differences in the laws which regulate their action from those which gravitation observes, have been ascribed to circumstances, which, in the one case, operate powerfully, but in the other can have little effect. The figures of the particles of matter have been supposed more particularly to have an influence of this kind on contiguous attraction, while the figures of masses of matter operated on at great distances can give rise to no appreciable result. This question is one which can scarcely be determined, since we are unable to estimate the force of those modifying circumstances which may exist; and the laws by which these attractions act, instead of being deduced from any assumption of the law of gravitation, must in the present state of the science be inferred from observation and experiment.

## CHAP. I.

## OF THE ATTRACTION OF AGGREGATION OR COHESION.

AGGREGATION is that species of attraction which unites particles of a similar kind. We perceive its action exemplified in a solid mass of matter, the parts of which cohere with a certain force, which resists any mechanical action that would produce their separation, and which, in different bodies, is exerted with very different degrees of strength. In liquids it appears to be weaker, or the parts are disjoined with much more facility: and in substances existing in the aerial form it is entirely overcome, the particles, instead of attracting, repelling each other. Bodies exist therefore in the solid, the liquid, and the aeriform state, according to the force with which the attraction of aggregation is exerted between their particles, and it is this attraction which unites these particles together.

Aggregation in bodies is weakened or overcome by two causes; by the repulsion communicated by heat, or by the attraction which may be exerted by the particles of one body to those of another.

Heat communicated to a solid body separates its particles to greater distances, as is evident from the enlargement of volume which it produces. By thus increasing the distances, the force with which the attraction of aggregation is exerted is weakened, and the repulsive agency of heat prevails: if the heat be carried to a sufficient ex-

tent, the aggregation is so far weakened that the body passes into the liquid form; and if carried still farther, the attractive force is entirely overcome, repulsion is established between the particles, and the body passes into the æri-form state.

The same effects are produced by the exertion of that attraction which unites the particles of one body with those of another. If a liquid, for example, be poured on a solid; it often happens that the attraction exerted by the liquid to the solid is sufficiently powerful to subvert the cohesion of the latter; its particles are disunited to combine with those of the liquid, and the solid entirely disappears. This forms the chemical process of Solution. A similar effect is sometimes produced by the chemical action of an æri-form fluid; and in some cases the mutual attraction, even of two solids, is such as to diminish the power of cohesion so far as to admit of their union, and the transition of the compound they form to a liquid state.

When these powers, whether of heat or of chemical attraction, are withdrawn, cohesion resumes its force; but with results which are different, according to the circumstances under which this happens.

When the attraction of aggregation is suddenly exerted, and with considerable force, the particles are united in general indiscriminately, and according to no regular law. If a body which has been melted is suddenly cooled to a sufficient extent, it becomes solid, and forms a mass of no regular structure or figure. Or if its cohesion had been suspended by the chemical attraction exerted by another body towards it, and if this attraction suddenly cease to operate, the force of cohesion is resumed, and the solid substance appears usually in the form of a powder. This lat-

ter case forms the chemical operation of Precipitation. A similar result is obtained, when, in consequence of chemical combination, a substance is rapidly formed, between the particles of which the attraction of aggregation is exerted with considerable force, at the moment of its formation.

But if the attraction of aggregation is exerted more slowly, the particles are united not indiscriminately, but usually with regularity, so as to form masses of regular structure and figure, bounded by plane surfaces and determinate angles. This forms the operation of crystallization, and such masses are denominated Crystals.

Crystallization may take place either from a state of fluidity produced by heat, or from a similar state produced by the exertion of a chemical attraction. Of the first we have examples in ice, which shoots in long slender crystals when water is cooled to a sufficient extent, and also in a number of the metals which have been melted, and then subjected to slow cooling. Of the second we have examples in many saline substances, which, when they have been dissolved in water, concrete in crystals, when part of that water has been withdrawn by evaporation, or when its solvent power is diminished by a reduction of its temperature. In any of these cases, if the operation is conducted slowly, so as to admit of the particles uniting by those sides most disposed to union, crystals are formed; and these are in general larger, more transparent, and more regular in their form, the slower the crystallization has been allowed to proceed.

The production of these regular forms is favoured by affording a nucleus, from which the crystallization may commence; and still more so, if this nucleus is of the same



matter as the substance to be crystallized, and is of a regular figure, the crystals are then, too, larger and of a more regular size.

The access of the air has an influence on the crystallization of some salts; a saturated solution, for example, of the salt named Glauber's salt; which has been inclosed while hot in a vessel, from which the air has been in a great measure expelled, not crystallizing when cold, but shooting into a congeries of crystals, the moment the air is admitted. The effect seems to depend on the sudden percussion from the admission of the air on the surface of the liquor, causing the approximation of the particles of the dissolved solid, whence the exertion of the attraction of cohesion is favoured; and hence any equivalent pressure applied in a similar manner has the same effect.

In this sudden crystallization is very well displayed a phenomenon, which always attends this process, the evolution of heat, the vessel in which it takes place becoming sensibly warm.

An enlargement of volume is often produced by crystallization, as in the example of ice, of several metals, and of a number of salts; while, in other cases, the reverse is the case, the volume of the crystallized substance being less than while it existed in the liquid state, differences evidently depending on the mode in which the particles unite.

Crystals formed from a watery solution generally retain a portion of water in a combined state. This is named their water of crystallization, and often amounts to half their weight: when deprived of it, they lose their transparency and density. Some part with it from mere exposure to the air, and suffer these changes: they are then said to *effloresce*: if they attract water and become humid, they

are said to *deliquesce*; but these properties of efflorescence and deliquescence are relative, and depend much on the state of the atmosphere with regard to humidity, so that a salt shall be deliquescent in a humid atmosphere, which is not so in one that is dry.

By the process of crystallization, substances may often be obtained separate which exist in the same solution. If one is less soluble than the other, it will after a certain extent of evaporation crystallize, while the other remains dissolved, and may be obtained by a subsequent evaporation: Or, if one is more soluble in hot than in cold water, while the other is nearly equally soluble in either state, the one will be obtained by crystallization when the liquor has cooled, while the other, when the necessary degree of evaporation has taken place, may separate while the solution is hot. The mutual attraction of substances dissolved together, sometimes, however, counteracts their crystallization; or causes each to crystallize with some intermixture of the other; and this, too, frequently alters the crystalline forms which either is disposed to assume.

Crystallization sometimes takes place in the transition from the aërial form, as is well exemplified in the arrangement of a flake of snow.

Every substance in crystallizing is disposed to assume a certain regular figure; sea salt, for example, assumes the form of a cube; nitre, that of a prism. The figure, however, is not invariable, but is liable to be modified by circumstances, and the same substance is therefore found under different crystalline forms.

The theory of crystallization is still obscure. It may be conceived that the particles of bodies are of certain regular figures, and that in uniting they may be disposed to ap-

proach by certain sides in preference to others, probably by those which admit of the most extensive contact. Hence a regular structure and figure, uniform with regard to each substance, will be produced.

The mechanical structure of crystals has been investigated with much labour by Haüy. He has shown that in every crystallized substance, whatever may be its actual form, there is a nucleus of a determinate figure, and which, by mechanical analysis, that is, by splitting the actual crystal according to its natural joinings, may be extracted. This nucleus or primitive form, he has also shewn, is constant with regard to each substance, however various the actual forms of its crystals may be; it may be farther subdivided, in certain directions, into more minute particles, and there is no limit to this possible subdivision but the composition of the substance. These form what Haüy denominates integrant particles; their forms are regular and invariable; their union constitutes the nucleus, or primitive form of the crystal, and by their super-position on this nucleus, according to certain laws, which Haüy has traced with much labour and ingenuity, the secondary forms, or actually existing crystals are produced. The development of this theory requiring extensive details, and being not strictly elementary, I may refer for the statement of it to my System of Chemistry.

The mode of describing the figures of crystals introduced by Werner, as subservient to mineralogy, is more simple. He assumes seven simple or principal forms, the icosaedron, the dodecaedron, the hexaedron including the cube and the rhomb, the prism, the pyramid, the table and the lens: and these are liable to the three modifications of truncation, bevelment, and acumination; truncation being that modification in which the angles

or edges of a crystal appear cut off and are replaced by planes; bevelment, that in which the edges, angles or terminal planes are so altered, that there appear two converging planes which terminate in an edge; and acumination, that in which, in place of the angles or terminal planes, there appear three or more converging planes terminating in a point or edge. To one or other of these forms, simple or under these modifications, all the actually existing figures of crystals may be referred; and though the method is an arbitrary one, and inferior to Haüy's in precision, it may be adopted as sufficient for the common purposes of description.

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CHAP. II.

## OF CHEMICAL ATTRACTION OR AFFINITY.

CHEMICAL Attraction is that force by which the particles of *different* bodies are united intimately ; the result of this union being not a mere aggregate or mixture, but a substance in which new qualities are acquired, the properties of the bodies combined being more or less changed. The term Affinity has been used to denote the same power, from an opinion, that some peculiar relation or resemblance exists between those bodies, which exert this mutual attractive force ; and the term, though derived from a groundless hypothesis, may, without any reference to its origin, be conveniently used as synonymous with chemical attraction.

The immediate result of the exertion of chemical attraction between two or more bodies, is the intimate union or assimilation of their particles, so as to form a homogeneous mass. This result is in chemical language named *Combination*. It is to be distinguished from *Mixture*, in which the particles, however intimately they may be blended, still exist apart, so that they are capable of being recognised, and of being separated by mechanical operations. It is also to be distinguished from *Aggregation*, which is only the union of particles of a similar kind, forming an aggregate which has the general properties of the particles of

which it is composed, whatever may be its mechanical structure or form.

The substance formed by chemical combination is named a *Compound*: the substances of which it is composed are its *Component* or *Constituent Parts* or *Principles*. When these are separated from their state of combination, the process is named *Decomposition*. If decomposition has been performed more peculiarly with the view of discovering the composition of a body, it is named *Chemical Analysis*. *Simple* or *True Analysis* is that case in which the principles of a compound, separated from their state of union, are obtained pure and insulated. *Complicated* or *False Analysis* is that case in which the composition is subverted, but the constituent principles have entered into new modes of combination, and formed therefore new products. If the decomposed substance is reproduced by the union of its constituent parts, the operation is denominated *Chemical Synthesis*. The *Integrand particles* of a body are understood to be the most minute parts into which it can be resolved without decomposition: they are of course similar to each other, and to the substance which they form. The *Constituent particles*, again, are those into which it is resolved by decomposition, which are therefore of a different nature, both with regard to the substance itself, and with regard to each other. It is between these that chemical attraction is exerted, while aggregation is conceived to be exerted between the integrand particles of bodies. In a chemical point of view all bodies are divided into simple or elementary, and compound,—into those incapable of being resolved into dissimilar particles or particles of different kinds of matter, and those which are capable of suffering such a change. The term *Element* in chemical language

is not however understood to imply a body essentially simple, but is applied merely to those bodies which have not been decomposed.

The theory of chemical attraction is still far from having attained perfection, though it has been the subject of much investigation. Newton suggested the idea, that the phenomena of chemical combination and decomposition might be owing to an attraction exerted between the particles of bodies, and varying in its force. This view was soon adopted by chemists. The elder Geoffroy endeavoured to ascertain the relative degrees of strength with which attraction is exerted among bodies. The subject continued to be prosecuted, until a number of observations more or less exact were accumulated, which Bergman reviewed, and placed in a clearer light. Berthollet has presented some novel views, interesting both in their application to minute phenomena, and in their relation to the theory of affinities. Some important general results have been established by the researches of Richter and Gay-Lussac. And the law, that attraction is exerted between bodies so as to combine them in definite proportions, first fully illustrated by Dalton, and of the highest importance if established in all the extent that has been given to it, forms at present an interesting subject of discussion.

From these preliminary observations and definitions, we may proceed to the more full statement of the doctrines of chemical attraction, generalizing these as far as the present state of our knowledge admits.

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SECT. I.—*Of the Phenomena which arises from the exertion of Chemical Attraction.*

THE immediate result of the exertion of chemical attraction between bodies, is their intimate union or combination, forming a new substance or mass perfectly homogeneous. This compound may exert attractions to other bodies, either simple or compound, and thus an extensive series of compounds may be established, and an immense number of bodies different from each other formed.

The most general phenomenon attending combination is a change in the properties of the bodies combined. The secondary qualities of bodies depending on the peculiar arrangements of their particles, it is easy to conceive, that when these arrangements are subverted, the properties must be altered, and that in the formation of a new substance new qualities must be acquired. Chemical combination is accordingly, in general, attended with very striking changes of properties; so striking, indeed, that we can seldom infer with certainty, from our knowledge of the properties of any body, what will be the properties of the compound it forms when united with another.

Still the entire change of properties from combination is not an invariable result. There are many cases in which they are only modified; and in some cases, as for example in the combinations of salts with water, so slightly so, that there is scarcely any evident change, but the change of form, which constitutes solution.

From considering this latter class of facts, it was former-



ly inferred as a general law, that the properties of compounds are derived from those of their constituent principles, and are intermediate between them ; while from attention to the former class of facts, the opposite doctrine has been stated in rather too unlimited terms, that the properties of bodies are always changed by combination. Berthollet has given a view of this subject, which in some measure reconciles these apparently opposite results. The properties of bodies, he supposes, would always remain in their combination, but for certain causes foreign to the combination itself, by which they are modified, and in some cases entirely disguised. Thus, there are properties which are incompatible, different tastes or colours, for example, which cannot exist together, and which must therefore neutralize or modify each other. From the approximation of the particles, which is the effect of combination, changes must be produced too in the secondary qualities depending on their arrangement. The same cause must give rise to modifications of chemical properties ; for if in consequence of this approximation, much cohesion is acquired, this must counteract the affinities of the principles of the compound, and render its action less energetic : and, on the other hand, if, by the condensation attending chemical union, the bodies uniting have passed from the æriform state to the liquid form, this, by removing the obstacle which elasticity opposes to their chemical action, may facilitate that action, and render it more extensive and powerful. Lastly, the diminution which is produced by the reciprocal force itself that unites two bodies, in the affinities which either of them exert to others, must cause the chemical action of compounds to be in general weaker than that of their constituent principles : this may in certain cases be modified by

the other causes which operate ; but still it is a general result, and in the successive combination of compounds, the ultimate product is usually a substance which exerts very feeble affinities.

Thus we perceive, that notwithstanding the changes that attend combination, the theory may be just, that the properties of bodies combining would always be discoverable in the compound, were it not for the operation of modifying circumstances. And we derive the rule, which in general will be found to hold true, that where energetic affinities are exerted, or where substances having opposing properties are combined, the properties will be materially changed ; but where the affinity is not powerful, and therefore the combination not very intimate, or where the substances combined are such as agree in the general assemblage of their qualities, the properties of the compound will not be very remote from those of its more active ingredient, or from the mean of those of its constituent parts. Even in very intimate combinations, we can often trace the properties of compounds from those of their component parts ; as, for example, the high refractive power of water, from its inflammable ingredient,—a property which led Newton to his singularly acute conjecture, that it contains an ingredient of that nature. The comparative volatility of compound salts, which are formed of principles disposed to assume the elastic form, affords a similar example.

In those combinations in which the changes of properties are least considerable, there is generally one change to be discovered to a greater or less extent, and which may even be regarded as a test of chemical union,—a change of density, the density of the compound never being the mean of the densities of its component parts. In the greater

number of cases the density is augmented, and sometimes to a great extent. In other cases, however, it is diminished, or the volume is enlarged.

As in chemical combination the particles of two bodies are made to approximate, we might expect that condensation would be always the result; and it is not very obvious how enlargement of volume should sometimes be produced. Berthollet has very well explained this. The immediate effect of combination is in every case condensation; but if the consequence of the combination is, that one of the bodies changes its form from the solid to the liquid, the enlargement of volume which attends this change of form may more than counterbalance the condensation from the combination; and hence, on the whole, diminution of density will be the result. It is accordingly in cases of solution, or where a solid body is acted on by a liquid, so as to be brought into the liquid state, that the exceptions to the more general law are observed. It must be added, however, that they are not altogether confined to these, but that sometimes there is enlargement of volume, even when the compound exists in the solid state, as in the combinations of some of the metals. When this happens, it is probably from a crystalline arrangement, which the particles of the solid assume in becoming solid, and is similar therefore to the increase of volume which attends the congelation of various substances.

In the combination of aerial substances, it has been stated as a general law by Gay-Lussac, that the condensation bears a certain simple proportion to the volume of the two airs, or rather to that of one of them, being generally exactly equal to the whole volume of one of the airs; sometimes it is double that of the volume of one, and sometimes

there is no apparent condensation whatever, the volume of the compound being exactly equal to that of its two ingredients. In the case of an aerial substance combining with a solid, the new compound existing in an aerial form, it happens in a number of cases, that the volume of this is exactly the volume of the aerial ingredient, so that the solid is received as it were into the air, and adds merely to its density.

A change of temperature, in other words the production of heat or cold, is, next to the change of properties, the most important phenomenon attending chemical combination. The production of heat is the more frequent change: it is often intense, and the great source of heat in the operations of art is chemical combination. Cold is also not unfrequently produced. It very generally is the consequence of the solution of saline substances in water, or in other more active liquids, and is still more intense in the mutual action of salts, and snow or ice.

Wherever a production of heat is observable in chemical combination, we can trace an increased density accompanying it; and the evolution of heat may be ascribed to this, since mechanical condensation is always a source of heat. On the other hand, where cold is produced in chemical action, there is always an enlargement of volume, to which, therefore, the cold may be ascribed. But the production either of heat or cold, from chemical action, is not strictly proportional to the change of density. Allowing the latter, therefore, to be the cause of the change of temperature, there must be some other circumstance by which it is modified. This is the change of form. It is sufficient, at present, to state, that when a body passes from the aeriform to the liquid state, or from the liquid to the

solid state, it gives out heat, and in the opposite changes absorbs it, in quantities not proportional to the degree in which the density is altered by the form; and hence such transitions of form, when they accompany chemical action, which they frequently do, modify the production of heat or cold which arise from the condensation attending the combination itself. By taking into consideration these two circumstances, the production of heat or cold from chemical action is explained with more precision than if one of them only were admitted in the theory; and there can be no doubt, that both, when they occur, have a share in producing the change of temperature.

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SECT. II.—*Of the Circumstances by which the exertion of Chemical Attraction is influenced.*

CHEMICAL attraction is not an invariable force, which, as exerted by any body, operates in all cases with the same strength. Its exertion is powerfully modified by circumstances foreign to it. Of these we can distinctly trace the influence of quantity of matter, cohesion, insolubility, specific gravity, efflorescence, elasticity, and temperature.

1. QUANTITY OF MATTER. The influence of this circumstance has been first illustrated clearly by Berthollet. Some of the facts from which it has been inferred had been known to chemists, and in the explanations given of these some approximations had been made to the principle itself. By Berthollet, however, it has been more fully developed, and more extensively applied.

The principle is, that the increase in the relative quan-

tity of a body exerting an attraction to another, adds to the energy of its action. The most direct proof of this is derived from the fact, that a compound may be decomposed if a large quantity of a substance exerting an attraction to one of its principles be made to act upon it, while from the action of a smaller quantity of the same substance no decomposition ensues. Of this there are many examples in chemistry, particularly in the decompositions of compound salts.

Another proof of it is, that a substance having an affinity to one of the principles of a compound, comparatively weaker than the affinity which they exert to each other, can produce a partial decomposition of the compound, if it be brought to act on it in large quantity; the increase in its quantity in some measure compensating for the weakness of its affinity.

Lastly, what is in conformity to the same law, if a compound is submitted to the action of a substance, exerting an attraction to one of its principles, even stronger than the attraction which unites them, still the decomposition is often only partial: a portion of the principle abstracted by the decomposing substance remains combined with the ingredient with which the entire quantity of it was combined in the compound; for, in proportion as the decomposition goes on, the increase in the relative quantity of that ingredient adds so much to the force of the attraction it exerts to the principle abstracting from it, as to be able to counterbalance the attraction producing the decomposition, and therefore to suspend its action. Hence there is a partition of the substance attracted, between the two bodies exerting attractions towards it; and the proportions in which this partition takes place, are determined as much

by the differences in the quantities of the bodies, as by the difference of energy in their affinities.

From these general facts, Berthollet has drawn the conclusion, that affinity is modified by quantity of matter, or, more precisely, that the chemical action of any body is exerted in the ratio of its affinity and quantity. The law, if admitted, is one of much importance in its applications, enabling us to explain with more precision many cases of chemical combination and decomposition; and illustrating the operation of some of the other circumstances which influence chemical attraction.

The facts, however, from whence it has been inferred, have been explained on a different principle. Bodies, it is maintained, combine only in a few definite proportions; in other proportions, with regard to each other, they do not unite: quantity of matter, therefore, cannot influence attraction to an unlimited extent; for if the quantity of any body exceed that proportion in which it is disposed to combine with another, it can evidently have no effect, nor can any effect arise from quantity in any proportions intermediate between those to which the combination is limited. All that can be inferred, therefore, is, that bodies uniting in certain definite proportions, the attraction between them is exerted with more force in one proportion than in another. And on this principle the facts, whence the general conclusion drawn by Berthollet is founded, have been attempted to be explained. The explanations will often be found, however, to be hypothetical, resting on the assumption that definite proportions are observed in combinations in which there is no proof that this is the case, and in which even the results themselves appear to preclude such a supposition. And the principle on which they rest, that

the strength of attraction between bodies varies when they are in different proportions to each other, is an admission even of the influence of quantity of matter on the force of chemical affinity.

2. COHESION. Cohesion is that force by which the integrant particles of a body are held in union : it must therefore counteract the action of any power, the tendency of which is to separate these particles, in order to bring them into new arrangements or combinations. Hence it powerfully modifies the exertion of chemical attraction ; and from the opposition of these two forces, in different degrees of energy, arise numerous shades of combination, more or less intimate, as the one predominates over the other, from the mere adhesion of the surfaces of bodies, or the absorption of a liquid into the interstices of a solid, to the most perfect chemical union. If cohesion be powerful, a strong affinity may be effectually resisted, and no combination take place. If cohesion be inconsiderable, a weak affinity may be predominant, and a combination be effected. And whatever diminishes the force of aggregation, favours the exertion of chemical attraction.

From the influence of this circumstance in counteracting combination, bodies in the solid state seldom act chemically on each other, whence the axiom was established in Chemistry, *Corpora non agunt nisi sint soluta*. To this there are exceptions, as in the action of various compound salts on each other, producing mutual decomposition, though both are solid, or in the action of some of these salts on ice or snow, even at very low temperatures. Yet still, in general, fluidity is necessary to chemical action ; and if not possessed by either of the bodies which are designed to act on each other, it is necessary that it should



be communicated, either by the application of heat, or by the previous operation of a solvent. Hence fusion and solution are the common *media* of chemical action.

Cohesion, existing in liquids to a certain extent, may counteract their mutual attraction where this is weak, though in general the resistance it opposes is so inconsiderable, that liquids combine readily, and in all proportions.

To these views, with regard to the effect of cohesion on combination, Berthollet has added some others, more novel, and equally important. He regards it not merely as a quality of bodies actually solid (or remaining in a slight degree in liquids) resisting the exertion of affinity, and ceasing to act when solidity is destroyed; but as a force which continues to operate when it has been apparently overcome, or when its effects are not sensible, and which, by a progression in its action, may at length influence combination. It may be suspended by a superior affinity, or by the agency of heat; and its energy may be so far subdued as to appear negative; but still it continues so far active, that if the forces by which it was weakened are diminished, its action will be exerted even before solidity takes place, and will counteract affinity. Or if, in consequence of new affinities, combinations are produced, it may determine the proportions in which the elements are combined; for being exerted between the integrant particles resulting from the combination, whenever its intensity is sufficiently powerful to counterbalance the affinity of the liquid in which these are formed, it will give rise to precipitation or crystallization, will of course withdraw the substance formed from the sphere of action, will oppose an obstacle to any further exertion of chemical power, and by such operation may determine the proportions of the combination. This effect, resulting from cohesion, will require

to be stated more fully in considering the limits to the exertion of attraction.

3. **INSOLUBILITY.** This property is merely the effect of cohesion in a solid, considered in relation to the liquid in which it is exerted, and of course its operation is similar. It opposes a resistance to the exertion of any attraction towards the body possessed of it, and it is an obstacle to the progress of combination, beyond that stage at which the insolubility withdraws the substance formed from the sphere of attraction. It equally favours decomposition, by withdrawing the ingredient of the compound which is precipitated, and thus removing it from counteracting the action of the decomposing substance.

4. **SPECIFIC GRAVITY.** Much difference of specific gravity in two bodies is an obstacle to their mutual union, since it is a cause favouring their separation, and of course a more powerful affinity is required to produce their union, than if such a difference did not exist.

5. **EFFLORESCENCE.** The operation of this circumstance, in influencing chemical action, is comparatively trivial, yet it sometimes can be traced. In mixtures of saline substances, a substance evolved or formed by their mutual decomposition sometimes rises on the surface in a loosely aggregated mass or congeries of minute crystals, forming what is named an Efflorescence. It is thus withdrawn from the action of the other substances, and this may contribute to the progress of the decomposition, or allow it to become more complete. Its influence has accordingly been observed in some important cases, particularly in the decomposition of sea salt by calcareous matter, and the production, both natural and artificial, of carbonate of soda.

6. **ELASTICITY.** The property of elasticity is possessed,

in such a degree, as to influence chemical action only by substances in the aërial form. In that form, the particles of a body are mutually repellent; and they are thus placed at great distances from each other. When two aëriiform bodies, therefore, are presented to each other, their particles are at distances too great to admit of the exertion of chemical attraction, so as to bring them into intimate union. Hence elasticity is generally an obstacle to chemical combination. In some cases where the mutual attraction is strong, the elasticity is overcome, and two aëriiform bodies combine together; but more generally the reverse is the case, or the attraction does not operate.

In conformity to this view, those circumstances which repress elasticity favour the combination of elastic fluids. Mechanical pressure, strongly and suddenly applied, causes them to combine. Rarefaction, on the contrary, prevents this: hence inflammable elastic fluids, in a certain degree of rarity, cannot be made to enter into that combination which constitutes combustion. The application of cold, especially when aided by pressure, has a similar effect in promoting combination. What appears singular, heat often gives rise to the same result; its operation, however, which is afterwards to be considered, may be reconciled to the same principle.

In the combination of an elastic fluid with a body not possessed of elasticity, as a liquid, the obstacle to their union is less; it generally therefore takes place more readily, at least to a certain extent. Still, however, the elasticity operates, and places limits to the quantity of the aëriiform body which the liquid absorbs. Hence this quantity is increased by whatever counteracts this force, as by the application of pressure. Cold has a similar effect, though the operation of this is in some measure counteracted by the

cohesion it communicates to the liquid ; and if this is carried so far as to produce solidity, the absorption of the aëriform body is not only counteracted, but the quantity which had been absorbed is often, at the moment of congelation, disengaged. In this way we can account for the fact, which otherwise appears anomalous, that the application of heat, especially if sudden and intense, often favours the combinations of aëriform with solid substances ; the diminution in the cohesion of the solid more than counterbalancing the augmentation of elasticity in the other.

Since elasticity in general counteracts combination, it may easily be understood that it will favour decomposition. If a compound consist of a solid ingredient, and of another, which, when uncombined, exists in the aërial form, it will be less difficult of decomposition, either by the application of heat, or by the action of another substance upon it, than if it were composed of two non-elastic bodies. If exposed to heat, the elastic ingredient, being disposed to acquire the state of elasticity, its affinity to the other is weakened, and it is at length expelled. Or, if the compound be submitted to the action of a substance which exerts an affinity to its non-elastic ingredient, this, in conformity to the usual law, weakens the affinity exerted between this and the other ingredient, and allows a portion of the latter to assume the elastic form. This again being thus withdrawn from the sphere of action, opposes no resistance to the action of the substance by which it was displaced, and therefore does not counteract the progress of the decomposition. Hence the decomposition of such compounds is in general more complete than that of those composed of inelastic substances, the substance excluded in the latter still continuing to act in opposition to the one by which it has been displaced, and the substance to which both exert an affini-

ty remaining in combination with portions of each of them.

7. TEMPERATURE. Temperature denotes the state of bodies with regard to heat and cold: much of its effect on chemical action is to be ascribed to the operation of some of the preceding causes, and particularly to the changes which these states occasion in cohesion and elasticity. Being in general complicated, however, and giving rise to peculiar results, it requires to be considered apart.

The application of heat usually favours chemical combination, there being numerous examples where two bodies do not combine at a low temperature, but enter into combination when their temperature is raised.

When the combination of solid substances is favoured by heat, the result is obviously to be ascribed to the diminution which the heat produces in the state of cohesion, this removing an obstacle to the exertion of their mutual affinity. Where it favours the combination of a solid with a fluid, or even with an aëriform body, as it frequently does, its operation is still similar, the cohesion of the solid being weakened, and the resistance which that cohesion opposes to the combination of its particles with those of the other substance being so far removed: though in this case, the result is rendered more complicated by the circumstance, that while the heat diminishes the cohesion of the one ingredient, it increases the elasticity of the other. This sometimes counteracts the combination, especially where the mutual affinity is not strong.

A very peculiar fact, and which appears at the first glance not to accord with these views, is, that heat favours the combination of elastic fluids. If two bodies each in the aëriform state are mingled together, it often, indeed, ge-

nerally happens, that no combination takes place. But if heat be suddenly applied, as, for example, if a burning body or an ignited spark be introduced into the mixture, they instantly combine. Here the result appears anomalous: the obstacle to the combination of substances in the aërial form is their elasticity, and the distances at which, in consequence of this, their particles are placed. By applying heat, this is increased, and the combination, instead of being facilitated, it might be supposed would be counteracted.

Is the following hypothesis adequate to the solution of this difficulty? When an ignited spark is introduced into the mixture, the space on which it falls has heat communicated to it, whence an expansion, proceeding from that space, is produced; and this expansion, by the pressure it must occasion on the surrounding particles, will cause them to approximate, and thus to unite. The whole effect is instantaneous, and it is on this that it depends. Were the heat to be slowly applied, and gradually raised, it would be diffused through the mixture, and the particles would be merely separated to greater distances. But a single point being heated to a high degree, while the surrounding particles remain at their usual temperature, the expansion from the former must press on the latter suddenly, and more quickly than the heat can be communicated. These, therefore, instantly approximate within the space at which chemical attraction is exerted, and their union is effected. The result of the combination is a farther evolution of heat, successively but rapidly taking place, which produces a similar effect on the contiguous particles, until the combination is complete. There are some cases, however, in which so little heat is extricated, that the introduction of a single

spark is insufficient, and therefore a succession of sparks must be applied.

The application of heat, in particular cases, favours decomposition as well as combination. Where, of the substances combined, one is more disposed than the other to pass into the elastic form, this tendency is favoured by a high temperature, and frequently so much so, that their mutual affinity is overcome, and decomposition ensues. By a similar operation, heat aids the decomposition of such compounds, by the affinity exerted by a third substance to the more fixed ingredient, and it often promotes the mutual decomposition of two compounds, favouring the union of the two more volatile ingredients, and thus allowing the attraction between the ingredients, which are comparatively fixed, to operate with effect.

In all cases, then, in which heat favours chemical action, it does so by the changes it occasions in the cohesion, or in the elasticity of the bodies concerned; but these often modify each other, and hence it often gives rise to apparently opposite results; it is therefore only by considering it in relation to both, that we obtain a just theory of its operation.

The same view is to be taken of the operation of cold. By diminishing elasticity it sometimes favours combination; and in other cases, by increasing cohesion it may counteract this, and give rise to decomposition. Or the one of these effects may modify the other, and thus give rise to results, which, were the joint action not attended to, would appear anomalous.

From the influence of the circumstances by which chemical attraction is counteracted, the corollary follows, that it cannot be affirmed in any case that bodies have no at-

traction to each other. There are many examples in which bodies do not combine, as in the familiar one of oil and water; but it is obvious, that since combination is in no case the simple result of the exertion of attraction, but always of attraction prevailing over cohesion, elasticity, or specific gravity, we cannot affirm, from combination not taking place, that no mutual attraction exists. All that can be inferred is, that the attraction is not sufficiently strong to overcome the opposing forces. It is difficult to conceive of attraction otherwise, than as a force with which every particle of matter is endowed, and which is exerted to every other; and the theory is evidently superior, which supposes this power, in particular cases, to be prevented from being efficacious, by the interference of extraneous forces, to that which supposes, that between certain substances it is altogether wanting, especially since in all cases the action of such forces can be demonstrated, at least to a certain extent, which may be sufficient to account for the result.

From the influence, too, of these circumstances, combined with the admission that all bodies have mutual attractions, it follows, as a probable conclusion, that the affinities exerted by compounds are the affinities of their constituent principles, modified by the circumstances under which they are exerted. It has been conceived, that when two bodies unite so as to form a compound, they form by their union the integrant particles of the compound, from which particles any chemical attractions belonging to it are exerted. It has also been supposed, that between these integrant particles of the compound, the cohesive attraction is exerted, which gives it its peculiar form. This, however, is rather an hypothesis by which the che-



mical actions exerted by a compound as such are represented with more facility: the aggregation, and even the chemical attractions, may be merely the result of the modified elementary affinities. It is no doubt true, that the affinities exerted by the compound are often extremely different from those of its elements: it combines with substances to which they appear to have no attraction, and it refuses to unite with others with which they form intimate combinations. But this may be expected from the different conditions under which they operate, and it is perhaps possible to point out how they may be diversified by circumstances, the influence of which is undoubted.

Thus, from the affinity which one of the elements of a compound exerts to the other, the affinities of either to other substances must be so far counteracted, and hence the cause of what is generally the case, that the attractions exerted by a compound are less powerful than those of its constituent parts, and that the ultimate products of successive combinations are usually substances having little energy of chemical action.

This, however, may be modified by other circumstances attending the combination, which may either concur with it, and still farther weaken the affinities of the compound, or which may counteract it, and render them more energetic. Thus, if a substance, by combination, pass from the solid to the liquid state, it acquires the advantages derived from fluidity, and its affinities, formerly counteracted by its cohesion, may now, notwithstanding some diminution which they suffer from the combination, be exerted with more effect. Or, if elastic substances by combination form a liquid, the advantage gained from this condensation and removal of elasticity may more than counterbalance the di-

minution of force from combination, and may render their affinities more extensive and more powerful. Or the reverse of these modifications may happen. If the result of a combination be the transition of a substance from the liquid to the solid state, the cohesion acquired will add to the diminution of its affinity from the combination itself; or if an aëriform compound be produced, the elasticity of this may concur with the effect of the combination in weakening the energy of its action.

With these views, many facts in the details of Chemistry strictly correspond, and they afford some happy explanations of chemical phenomena. Affinities thus modified, Berthollet has named *Resulting*, to distinguish them from the affinities of the immediate principles of a compound, which, in contradistinction, he names *elementary*.

To this head of *resulting* affinity, may probably be referred those anomalous cases of chemical action which have been classed together under what has been named *Disposing* Affinity. In all these cases, the decomposition of a compound, and the combination of one of its elements with the substance producing the decomposition, is promoted by the action of a third substance, though it exerts no sensible attraction to either of the bodies the combination of which it thus promotes. It has been observed, however, that it always has an attraction to the compound they form, and to this attraction the effect has been ascribed,—a solution of the difficulty which appeared very absurd, as it supposes the attraction of one body to another, not in existence, to be the cause of the latter being produced. The compound must be formed before any affinity to it can be exerted. This conclusion appears to be just. But if, according to the preceding doctrine, all bodies have mutual

affinities, and if the affinities of compounds be the modified affinities of their elements, the affinity between the *disposing* substance and the compound is of course the modified affinities of the elements of the latter to the former : these may be exerted therefore previous to the combination, and concurring with the affinity which they at the same time mutually exert, may produce a union of forces whence the combination of the whole is established. It is probably from this union of dormant affinities, favoured more or less by the circumstances under which they are exerted, that all cases of disposing affinity arise.

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SECT. III.—*Of the Limits to the Exertion of Chemical Attraction.*

CHEMICAL attraction obeys certain limits ; *first*, with regard to the relative quantities in which it causes bodies to combine, and, *secondly*, with regard to the number of substances between which it may be exerted, so as to bring them into simultaneous combination.

*First*, In the greater number of combinations, there are limits to the attraction exerted, with regard to relative quantity ; or the bodies are not always combined in indefinite quantities, but often only in determinate proportions. Under the general proposition with regard to this, several classes of facts may be arranged.

1st, There are cases in which two bodies can be combined together only in one proportion, and if an excess of either ingredient of the compound be present, it remains

uncombined, with its properties unchanged. The constituent principles of water afford an example of this.

*2dly*, Attraction is frequently exerted between two bodies, as to combine them in two, in three, or even in four proportions; but these are always definite, so that in the intermediate proportions no combination is established. These combinations give rise to compounds which differ entirely in their properties from each other, the differences being frequently as great as if they were formed of principles altogether different. From this cause principally arise the diversities in the properties of the substances belonging either to the animal or vegetable kingdom, these consisting in general of the same principles, united only in different proportions.

*3dly*, Combination is sometimes unlimited to a certain extent, but when this is reached it is arrested. Water, for example, will dissolve any quantity of a salt up to a certain proportion; but when this has been combined with it, the mutual attraction ceases to operate with effect, and no larger quantity can be dissolved. The limitation of combination in this case is named Saturation; and when the water has dissolved the largest quantity of the salt which it can dissolve, it is said to be saturated with it.

*Lastly*, There are cases of combination absolutely unlimited, or in which bodies unite in every proportion. This is observed to happen principally in the combination of liquids with each other, where the compound retains the liquid form.

When combination takes place in determinate proportions, it generally happens that there is one proportion in which the properties of the bodies combining are mutually lost or neutralized; the distinctive properties of neither

ingredient appearing in the compound ; while in the proportions different from this, the properties of the ingredient which is in excess may be recognised, weakened only to a certain extent. The stage of the combination at which this happens is named the point of Neutralization, and sometimes the point of Saturation. The latter, however, is more properly employed in the sense already pointed out, as denoting the extreme of combination ; and the term Neutralization is preferable, as signifying that state in which the properties of the bodies are mutually lost or neutralized.

It is a question of some interest and importance, to what causes these varieties of combination are to be ascribed ; and it would be satisfactory to reduce them to one general principle. On this subject a theory was advanced by Berthollet ; to which has since been opposed a system precisely the reverse.

The principle of Berthollet's theory is, that affinity is a force always disposed to operate on bodies, and to unite them in whatever relative quantities they are presented to each other ; that any limits opposed to its exertion arise from external forces, cohesion, elasticity and others, by which it is influenced, and that it is only by the operation of these that determinate proportions are established. Hence where these external forces do not operate, as in the mutual action of two liquids, the compound remaining liquid, the combination is unlimited with regard to proportion. When cohesion or elasticity is present in the subjects of the combination, as in the action of a liquid on a solid, or in the absorption of an æriform substance by a liquid, these forces limit the quantity of the solid that can be dissolved, or of the air that is absorbed,—the affinity producing the

the combination becoming weaker as the combination proceeds, while the cohesion of the remaining solid, or the elasticity of the unabsorbed air, continues as at first, and therefore an equilibrium must be arrived at, when the combination will cease. Up to that period it takes place in indeterminate proportions; but when it is reached, a limit is placed, beyond which it cannot proceed. And, lastly, when, in the progress of combination, the result in any part of it is great condensation, this by the obstacle it may oppose to the exertion of affinity, or even from the greatness of the condensation, by withdrawing the product from the sphere of action, may limit the combination to that point, or to the proportion at which this effect is greatest; or if, by particular circumstances, this is overcome, in the further progress of the combination it may again happen; and, in this way, compounds, in two or three determinate proportions, may be formed.

The opposite doctrine rests on the principle, that it is the tendency of chemical attraction to combine bodies in definite proportions, independent of the operation of external circumstances; and what constitutes a leading feature of the doctrine, it is farther maintained, that where a body combines in different proportions with another, these proportions have simple arithmetical relations to each other. This view was first distinctly presented by Mr Dalton. Where two bodies combine only in one proportion, they probably unite, he supposed, atom to atom singly: Where they combine in two proportions it is probable that the combination in one proportion is that of atom with atom, in the other of one atom with two atoms; and combinations may in other cases take place in the proportion of one with three, or one with four, or even in other sim-

ple proportions. The following short table represents the order in which two bodies, A and B, may thus be supposed to combine, forming the products or compounds denoted by C, D, E, &c.

- 1 atom of A + 1 atom of B = 1 atom of C, binary.
- 1 atom of A + 2 atoms of B = 1 atom of D, ternary.
- 2 atoms of A + 1 atom of B = 1 atom of E, ternary.
- 1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
- 3 atoms of A + 1 atom of B = 1 atom of G, quaternary, &c.

A similar principle was stated by Dr. Wollaston: . He had observed in certain cases of decomposition of saline compounds, that the quantity of one of the ingredients, separated by a partial decomposition, is exactly half the quantity of it which the compound contained ; --that if the compound, for example, of an aërial with a fixed substance were exposed to heat, a certain quantity of the former was expelled from it, and if after this it were submitted to the operation of a more powerful chemical affinity, so as to undergo complete decomposition, it yielded another quantity of it precisely equal to the former. This seemed to shew that the fixed body combined with the other in two definite proportions, the one proportion being double of the other. And from a number of facts of this kind, Dr Wollaston drew the conclusion, that the elements of bodies are disposed to unite atom to atom singly, or if either is in excess, it exceeds by a ratio to be expressed by some simple multiple of the number of its atoms.

Gay-Lussac has observed a relation in the combinations of aërial bodies, which leads to the same principle. Some of these were known to combine in simple proportions

with regard to volume, as that of equal volumes, or that of two volumes of the one body to one of the other. Extending his researches to the greater number of the combinations of this class, he has shewn that this is a general law with regard to them,—that elastic fluids combine in ratios the most simple, those of 1 to 1, 1 to 2, or 1 to 3 in volume. This view of the subject has one peculiarity distinguishing it. When the proportions of the elements of a compound are estimated by weight, there is no simple proportion between them in the first combination: it is only when there is a second combination of the same elements that the additional portion of one of them is a multiple of the first; but in elastic fluids, even in the first combination, the two elements have a certain simple proportion to each other.

In proof of the doctrine of combination being established in definite proportions, a number of analytical results have been given by Berzelius, who has farther carried to a greater extent than any other of its supporters, the hypothetical inferences which may be drawn from the general principle.

There is another form, too, under which the doctrine has been presented, in which it is connected with certain speculations as to the weight of the atoms of bodies. If it be admitted, that in the combination of two bodies in certain relative proportions, they unite atom with atom singly, or that they unite one atom with two, or with any other known number of atoms, then the relative weights of these atoms may be inferred from the relative quantities in which the bodies combine; for, taking the simplest of these cases for illustration,—that in which one body combines with another in one proportion, if it be assumed, as Mr Dalton



says it is reasonable to do, that the two bodies combine atom with atom, then the weight of these atoms must be as the quantities of the bodies which combine, since by assumption these quantities respectively contain the same number of atoms. Oxygen and hydrogen, for example, combine in one proportion, that of 7 or 7.5 of the former to 1 of the latter. It is assumed that this combination is a binary one, or that one atom of oxygen combines with one atom of hydrogen. The number of atoms of oxygen, therefore, in the quantity of it which enters into union, and the number of the atoms of hydrogen in the quantity of it which combines, are the same; hence the weights of these atoms must be in the ratio of 7 or 7.5 to 1. If we take one of these bodies as a standard, (and hydrogen is selected by Mr Dalton as the common standard), and state the weight of an atom of it as 1, the weight of an atom of oxygen will be 7, and on the same principle the weights of the atoms of other bodies may be determined. Mr Dalton has accordingly given an extensive system of this kind, representing the weights of the atoms of the more important chemical agents, and the constitution of a number of chemical compounds. Sir H. Davy has represented this in a different manner, by considering water as a compound in which two proportions of hydrogen are combined with one of oxygen; hence the number representing hydrogen being 1, that representing oxygen is 15, and the numbers applied to other bodies are changed in a similar manner. Others have taken oxygen as the unit, and have thus been led to assign other weights to the atoms of bodies, but still the system under these different forms is essentially the same.

It is obvious that this is altogether hypothetical. We

have no means of determining in any case what number of particles of one body combine with another. It is reasonable to infer, it is said, that in a combination taking place only in one proportion, that for example of oxygen with hydrogen, one atom of the one body combines with one atom of the other: Another, however, finds it more reasonable to infer, that in this combination two atoms of hydrogen combine with one of oxygen; and it is just as reasonable to believe, that two of oxygen combine with one of hydrogen, or that other numbers combine. The whole is mere assumption, and, were even the doctrine of definite proportions established, little advantage could accrue to the science, from connecting with it an hypothesis, and expressing its results in the language of that hypothesis, which might be stated with more simplicity and equal precision in another form.

Excluding this part of the doctrine, and comparing the two general systems, we find the fact demonstrated, that in many cases combination is absolutely unlimited with regard to proportions: in these, therefore, the principle of the one theory is established, while that of the other is excluded. In itself too it is more probable. It can scarcely be conceived but that attraction is a force which will be exerted between bodies in all relative quantities in which they are placed within the sphere of its action; it may be exerted more powerfully in some proportions than in others, and this may establish the combination in these proportions: but it is improbable that there are proportions in which it should not be exerted, and in which therefore, by peculiar arrangements of circumstances, combination may not be established.

Neither can the influence of external forces in deter-

mining the proportions in chemical combination be disputed. The operation of cohesion and of elasticity, in particular, in placing limits to it, where it would otherwise be unlimited, is in many cases sufficiently evident. Their influence even in establishing combinations in definite proportions is conspicuous in the striking fact to be afterwards noticed, that all the cases referred to superior elective affinities are those in which the force of cohesion is powerfully exerted, and insoluble compounds formed. The influence of relative quantity of matter on the force of chemical affinity, which is irreconcilable with the doctrine, that combination takes place in definite proportions, is not less established; and the facts which prove it cannot otherwise be accounted for, but by explanations more complicated, and resting only on hypotheticalal assumptions.

All, then, that can be strictly inferred is, that with regard to some bodies there is a tendency to combine in certain definite proportions with regard to each other. This may sometimes arise in whole or in part from the operation of external forces, of condensation in particular, insulating the compound at a particular stage of the combination. But it cannot always perhaps be referred to such a cause; nor is it easy to account, from the operation of external circumstances, for the law which appears to be observed, that where there are different combinations of the same elements in definite proportions, the additional proportions of one of the elements are multiples of the first. It is, on the other hand, sufficiently probable, that attraction may be exerted more forcibly between the particles of bodies when they are in certain relative quantities with regard to each other, and that this may give rise to the combinations being more easily established in these proportions, and being more perma-

nent than in others. But it does not follow from this, that in all cases there will be such tendencies; nor does the admission of the fact exclude the operation of these external circumstances by which attraction is influenced, and combinations are modified. Berthollet has accordingly shewn, that even in those cases in which definite proportions having simple ratios to each other exist, (the cases, for example, stated by Dr Wollaston), combinations of the same elements in other proportions may be formed; and he has farther shewn, that the strength with which attraction is exerted varies in these proportions, and that, conformable to the law that quantity of matter influences the force of attraction, the ingredient of a compound is retained with more force as the quantity of it becomes relatively smaller to that of the other ingredient with which it is combined.

The important point of investigation, then, in relation to this subject, is, to determine those cases in which definite proportions are observed, and those in which they are less strictly limited, resting this determination on actual experiment, and excluding the inferences which rest merely on hypothetical reasoning. If the law of definite proportions were strictly established, its importance is unquestionable, in the assistance it would afford to chemical researches:—the existence of a certain ratio, for example, between the known combinations of two bodies suggesting the existence of other combinations unknown, and leading therefore to their discovery, and the knowledge of such proportions being capable also of being applied to detect the errors of analysis. But if the law is less strictly observed, if it scarcely exists with regard to some bodies, and even if with regard to others, where it does operate in establishing definite proportions, it does not exclude other combinations, it is

evident, that the assumption of it must lead into error, give rise to fruitless investigations, and retard the progress of the science, by introducing hypothetical conclusions.

*Secondly*, Chemical attraction observes certain limits, with regard to the number of substances which it combines together. It not only unites two substances; it frequently brings three or more into combination.

When three substances are placed within the sphere of chemical action, it often happens that two of them combine, to the exclusion of the third, or one is combined with each of the others in proportions determined by their affinities and quantities. In some cases, however, instead of either of these varieties of combination, the three substances enter into simultaneous combination, and form only one compound. Even four, five, or perhaps more substances may be thus combined. Such combinations are named Ternary, Quaternary, &c. according to the number of their constituent parts.

There are numerous examples of these combinations among the metals. They occur also frequently among the salts, one acid being saturated by the joint action of two bases. Nature, too, presents us with a number of such combinations in the vegetable and animal systems. Nearly all vegetable substances are compounds of at least three principles; and the composition of the animal products is still more complicated, four or five principles being combined in their formation.

These combinations appear to take place principally where all the substances have mutual attractions, which, under given circumstances, do not differ greatly in force, and where the external forces of cohesion, &c. do not much

interfere. Were the attraction of one ingredient to any of the others much superior, it would probably give rise to an insulated binary compound; or did the force of cohesion or elasticity operate with much energy on any of the substances in their mutual binary combination, this might modify the reciprocal action. But where neither of these circumstances is present, the affinities may be balanced, and give rise to one combination. Hence, probably, their formation, more peculiarly in the vessels of vegetables and animals, where, from the motion and agitation under which they are placed, and the smallness of the mass in which the affinities operate, these circumstances are obviated, and this equilibrium of mutual affinities is established.

A law stated by Gay-Lussac appears to prevail in ternary combinations, that the elements are united in such proportions, that when the combination is subverted they unite two and two, one of the ingredients in certain portions combining with each of the others, and form binary compounds of determinate composition.

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#### SECT. IV.—*Of the Forces with which Chemical Attraction is exerted.*

BODIES exerting attractions to others, exert them with different degrees of force; and from this arises a series of important chemical changes.

From the attraction exerted by one substance to another, their combination takes place. But this attraction may be inferior in force to the attraction which either of these substances exerts to a third body. In this case, if

this body be brought to act on the compound which the others have formed, it will decompose it; the two which exert the strongest attraction will combine, and the third will be separated. Hence arises an extensive series of decompositions; and hence, too, is derived the power of the Chemist to recover in an insulated state, substances which have been combined together, as well as to obtain the principles of which natural compounds are formed.

The case now explained has been named *Single Elective Attraction*,—a substance combining with another apparently in preference to a third. It was usually supposed that this combination is exclusive, and that the substance which is displaced is obtained pure and insulated. In many cases, however, from the influence of quantity on affinity, the excluded substance retains a portion of the one with which it was originally combined; and in other cases it attracts a portion of the decomposing substance. And it is principally where the external circumstances, especially cohesion and elasticity, which influence chemical affinity, operate powerfully, that complete decomposition is produced.

Geoffroy, a French chemist, first endeavoured to ascertain the relative forces of attraction among the principal chemical agents. He represented them, so far as they were known, in a tabular form; and since his time the labours of many chemists have been directed towards correcting and extending these tables. Their construction is extremely simple. The substance whose attractions are to be enumerated, is placed at the head of a column, and the substances to which it has attractions are placed beneath it, in the order of their relative forces, the substance to which it has the strongest attraction being immediately under

it; the others following in that order, and the one to which it has the weakest attraction of course closing the column. Thus the attractions of lime and of muriatic acid are represented in the following tables :

| LIME.            | MURIATIC ACID. |
|------------------|----------------|
| Oxalic acid.     | Barytes.       |
| Sulphuric acid.  | Potash.        |
| Tartaric acid.   | Soda.          |
| Phosphoric acid. | Lime.          |
| Nitric acid.     | Ammonia.       |
| Muriatic acid.   | Magnesia.      |

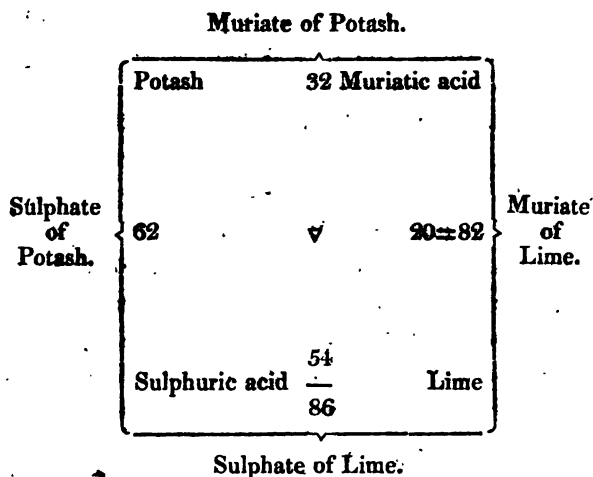
There is another case of elective attraction, more complicated: Suppose we have a compound formed by the union of two bodies A and B, and that to this compound another is presented composed of C and D; it often happens that the two compounds exchange their principles, A leaves B to combine with C, while at the same time B combines with D, and two new compounds are thus formed: and this decomposition is effected by these joint forces, while one of the compounds could not have been decomposed by the sole action of one of the ingredients of the other. Thus, if the force of attraction between A and B were equal to 20, and the attraction of C to A equal to 16, C alone could not have decomposed AB. But if the affinity of C to D is equal only to 7, while D exerts an attraction to B equal to 12, then a decomposition must be effected on mixing these two compounds; for the sum of their existing attractions is inferior to the sum of those tending to separate them; the former, the affinity of A



to B, and the affinity of C to D, being equal only to 27; the latter, the affinity of C to A and of D to B, being equal to 28.

This has been named Double Elective Attraction; two elective attractions being exerted, and two new compounds formed. Of the two attractions which are exerted, the tendency of the one is to preserve the original compounds undecomposed, that of the other is to separate their principles. The former were named by Kirwan the Quiescent; the latter, the Divellent Attractions. It is evident, that a double decomposition can only be effected, where the sum of the divellent is superior to that of the quiescent attractions.

Diagrams have been employed to represent these elective attractions. Dr Cullen employed one in which two cylinders crossed each other at the middle, and were supposed to be moveable, so that the two extremities brought together represented the union of the substances acted on by the attractive force. Bergman employed another, better adapted to represent the results and the circumstances connected with these decompositions. It consists of two brackets connected by straight lines, forming a square, at the sides and corners of which, the names of the existing compounds, and of their ingredients, are placed, as in the annexed figure.



If the two compounds, named Sulphate of Potash, and Muriate of Lime, the former consisting of sulphuric acid and potash, the latter of muriatic acid and lime, be mixed together, a double decomposition takes place, and two new compounds, muriate of potash, and sulphate of lime, are formed. This is represented by placing on the outer sides of the two brackets the names of the two compounds mixed, and at the corners of the brackets, the names of their ingredients, so disposed that the one acid shall be diagonally opposite to the other. If the numbers expressing the relative force of attractions of the principles of these compounds be also added, it will be obvious whether decomposition will ensue. If the attraction between potash and sulphuric acid equal 62, and that between lime and muriatic acid 20, the sum of the quiescent attractions will be 82. But if the attraction between potash and muriatic acid be 32, and that between sulphuric acid and lime 54, the sum of the divellent attractions will be 86. These, therefore, will

operate with effect ; the muriatic acid and the potash will combine together, as will the sulphuric acid and the lime ; and to represent this the names of these resulting compounds, muriate of potash and sulphate of lime, are placed without the straight lines, by which the brackets are connected.

To represent a single elective attraction, the same figure is used, with one bracket only.

Where the quiescent attractions are superior to the divellent, and where of course no decomposition takes place, the scheme consists of two unconnected brackets, with the names of the compounds at each side, and of their ingredients at each corner ; the numbers, denoting the forces of attraction, being interposed.

In these decompositions it frequently happens, that one or both of the new compounds prove insoluble, and consequently fall down. This is denoted by bending downwards in the middle, the line placed between the substance and the square, as in the diagram, where the undermost line is bent down to shew that the Sulphate of Lime is precipitated. If one of the substances be volatilized or sublimed, the line is bent upwards in the middle. If they are neither precipitated nor volatilized, the brackets are connected by straight lines.

Lastly, the circumstances under which the decomposition takes place, are pointed out. When it is effected by heat, this is denoted, by inserting in the middle of the diagram a triangle,  $\Delta$ , the old chemical symbol for fire ; and an inverted triangle,  $\nabla$ , the mark for water, is inserted when the decomposition takes place in a watery solution. The same method is still used, the signs only having been changed ; and to facilitate the construction of such dia-

grams, all the chemical agents have likewise been distinguished by particular symbols.

There is an important general fact with regard to these decompositions, that the state of neutralization in the compounds remains unchanged. If two compounds, in each of which the ingredients are combined to the point of mutual neutralization, be mingled together, and a double decomposition ensue, the two new compounds that are formed will be equally neutral;—a result which shews such a relation between the proportions of the substances, and their power of producing neutralization, that the quantity of one which neutralizes the base with which it is combined in the one compound, will, when transferred to the base of the other, neutralize the quantity of it which the ingredient detached from it had neutralized; while this, on the other hand, will be equally capable of neutralizing the quantity of base with which the other had been combined. It leads, as is afterwards to be stated, to an accurate method of determining the composition of saline compounds.

Such are the doctrines of single and double elective attraction, as they were delivered by Bergman. A different view has been given by Berthollet of these changes, which it is necessary to explain.

In Bergman's theory, affinity is regarded as an invariable force; and decompositions are ascribed to the different degrees of force with which it is exerted. In the theory of Berthollet, they are referred principally to the operation of those external circumstances by which attraction is influenced. If the substances which act on each other be liquid, or soluble in the fluid, which is the medium of action, and if the compounds they form in any

stage of combination have no great cohesion or insolubility, no evident change appears when they are mixed together; there is a mutual saturation, and the opposing substances remain united, forming a combination, in which the forces are balanced. But if, on any of the parts of such a combination, cohesion or insolubility, or elasticity operate with energy, these external forces subvert the balance, give rise to separations, and are the cause of the results which used to be ascribed to the predominance of strong over weak affinities.

Thus the effect of chemical combination is condensation. If substances are submitted to mutual action, some of which have a strong tendency to cohesion, and if in combining with others this tendency is increased by the condensation attending the combination, it may so far operate as to insulate the compound, and give rise to its separation, leaving other principles combined on which this external force operates with less effect. Thus, in a case of double decomposition, where four substances are presented to each other, if one of them has a tendency to pass into the solid state, and if this is increased by its combination with one of the others, so that they form a compound of sparing solubility, this may determine their combination, and the compound they form will be separated by precipitation or crystallization, the other two remaining in combination and in solution. If even these four substances were previously in the reverse binary combinations, the same extraneous force will cause an exchange of principles, or, when three substances are presented to each other, if the combination of two of them give rise to a substance of sparing solubility, or having a strong tendency to cohesion, this in like manner will determine their union, and cause the separation of the insol-

ble compound, instead of the balance of affinities which would otherwise have been the result.

Elasticity sometimes gives rise to similar effects, especially where heat is applied. An elastic ingredient, in single elective attraction, will, from this cause, be more easily displaced; and, in double elective attractions, it will determine the combination of the two opposing substances which are most disposed to assume the elastic form.

This view of what have been named *Elective Affinities* appears to be supported by a very extensive coincidence with facts,—those substances which, in decompositions effected by the medium of solution, have been considered as exerting the most powerful affinities, being those which form the least soluble compounds, and with regard to which, therefore, the force of cohesion appears peculiarly to operate; and those which, in decompositions effected by heat, have been regarded as exerting the weakest affinities, being those which have the greatest tendency to volatility, or which form the most volatile compounds, and on which therefore the power of elasticity must operate with greatest effect. The influence of both these forces must indeed be exerted in these as in other cases of chemical action to a certain extent; but there is some obscurity with regard to their mode of operation, if they are considered as the sole effective forces; and in considering them as such, it may be questioned whether Berthollet has not extended their influence too far. Differences in the forces of affinity as exerted among different bodies exist, and such differences must apparently have an effect, considerable even in determining the combinations which take place. It is difficult however to assign the relative importance of these causes, as it is not easy to determine how far the force

of cohesion itself in a compound is the result of chemical attraction, or what precise relation exists between these powers.

THE problem with regard to the absolute forces of affinities among bodies is one which Chemists have frequently attempted to solve. That attractions differ in force, as exerted by each body to a series of others, is sufficiently evident; the difficulty is to discover their degrees of strength. Were these known, many of the deductions of the science would rest on calculation; but this has hitherto been very imperfectly attained.

Several of the methods on which the solution has been attempted, rest on false principles. Guyton, observing that different metals adhere to the surface of quicksilver with different degrees of force, supposed that these might indicate their respective affinities to that metal,—a method not only limited as to the possibility of its execution, but inaccurate, inasmuch as the adhesion denotes merely the facility of combination, which depends as much on the cohesion of the metals as on their attractive powers. Wenzel had supposed that the quantity of a body dissolved in a given time by another, affords a measure of the force of the affinity exerted,—a principle equally defective, since the rapidity of combination depends not merely on the affinity, but on this modified by the other circumstances which influence chemical action. Neither can any results connected with the facility of decomposition of compounds afford any certain indications, since these are dependent to a certain extent on the same circumstances.

Kirwan observed a connection between the affinities of bodies and the quantities of them required to neutralize

the properties of other substances with which they combine; and Berthollet, correcting and extending his views, has advanced the principle, that the power possessed by a body of neutralizing the properties of another, is the result of the strength of its affinity to that body, and may therefore be regarded as a measure of it; the affinities of different substances towards another being in the inverse ratio of the quantities of them necessary to neutralize the properties of an equal quantity of that substance; in other words, the smaller the quantity of a substance required to neutralize another, the more energetic is its attraction towards it. To discover, therefore, the forces of affinity, as exerted by different bodies, it is only necessary to determine the quantities required to produce neutralization in those with which they combine.

On this principle, Berthollet has indicated the order of the affinities of the principal acids, and of the bases which they neutralize; and this order is very different from that inferred from the known series of decompositions. This, indeed, is no just objection against the theory; for these decompositions arising from the operation of other forces besides that of affinity, there are no grounds to infer that they shall correspond with the real scale of the forces of attraction. There is reason to doubt, however, whether the principle is altogether just; and, even if it were, the investigation is, in the present state of our knowledge, attended with such difficulties, that the results are far from being certain. We are unable also to appreciate the force of those circumstances by which the exertion of chemical attraction is modified; and we should derive therefore less advantage from a knowledge of the absolute forces of affinities were even this attained.



From the preceding observations, it must be apparent, that the common tables of elective attraction do not represent the relative forces of affinity, but only a series of decompositions, which arise from the operation of circumstances which influence attraction, as much as from differences in the strength of attraction itself. Nor do they even express the order of these decompositions with accuracy; since the influence of quantity, which so materially modifies the results, has been neglected in the experiments on which they are founded. They are therefore of less utility than has been believed. As they may be condensed, however, in a short space, and may sometimes be consulted, I have inserted them along with other tables in the appendix.

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## BOOK II.

### OF REPULSION, AND THE POWERS BY WHICH IT IS PRODUCED.

**T**HE attractions exerted between the particles of matter are counteracted by certain forces of repulsion, and by these the arrangements and combinations to which the former give rise are modified or subverted. Their operation, therefore, is important in the production of chemical phenomena.

Of these repulsive forces, the most general in its agency is the power of Heat, or Caloric. This power is present in all bodies : it is capable of being increased or diminished, and this increase and diminution are accompanied with corresponding changes in the distances at which the particles of bodies are placed. Electricity, especially under the form of Galvanism, likewise exerts a repulsive agency, and is even more powerful than heat in subverting chemical combination. With these agents, Light has an intimate connection. Its materiality is indeed more decidedly established, yet it is doubtful if it exert any chemical affinities ; its particles are mutually repellent, and it is not improbable, that in producing chemical changes, it operates by the repulsion it communicates to the particles of bodies. The materiality of caloric, and perhaps also of electricity, is more doubtful, and they are with most propriety considered in chemical arrangements as General Powers.

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## CHAP. I.

### OF CALORIC.

OF the sensations we experience, none are more familiar than those of heat and cold. These are excited by bodies applied to the organs of sense, and with regard to this, no fact is more familiar, than that the same body excites at different times very different degrees of these sensations. The inference from this is obvious, that the power of producing the sensation does not strictly speaking belong to the body applied, but depends on some principle or power which it contains, and which is capable of being increased or diminished; the increase or diminution of it in any particular substance being accompanied with corresponding changes in the power of producing these sensations. We thus arrive at the conclusion, that there exists a cause of heat,—a power or principle capable of being communicated to bodies, and of being withdrawn from them. We can observe the transfer of it from one to another; for by bringing a cold body into communication with a hot one, the latter communicates to the former, to a certain extent, its power of exciting the sensation of warmth, losing at the same time proportionally the power it has of exciting the same sensation: and this communication may continue to be made over any number of bodies, until an equilibrium is established.

It is scarcely necessary to illustrate this by example. A piece of iron, which has been heated, if plunged into cold water, loses a portion of its heat, which the water acquires; the water may equally be deprived of this, and the power be transferred to another body.

So far the idea of the cause of heat is limited. It has been farther extended by the observation of other effects which it produces. When a body is heated, it is also expanded, or its volume is enlarged in every direction; when it is cooled, the volume is diminished; and the diminution or increase of volume bears a general proportion to the abstraction or addition of the peculiar power on which these effects depend.

It has, lastly, been proved, that when this expansion is carried to a certain extent, bodies change their forms, solids becoming liquid, and liquids being converted into vapours or airs.

These effects being thus connected, are justly considered as arising from the exertion of the same power. It has been distinguished by different appellations; as Fire, Heat, the Matter of Heat, or the Igneous Fluid,—terms either ambiguous, or implying an hypothesis, and therefore superseded by the more unexceptionable appellation of Caloric.

By Caloric, then, is to be understood, a power present in bodies, the cause of their expansion, and of their conversion into the fluid and æriform states, and which, when present in a certain quantity, excites in animals the sensation of heat, the sensation of cold being also the effect of its abstraction.

Some have considered this power as a peculiar subtle fluid diffused over matter, and capable of entering into eve-

ry body; others have supposed all the phenomena exhibited by heated bodies to arise from a peculiar state of these bodies,—a vibratory motion, more or less violent, of their minute particles. The question on this subject will be more properly examined after the effects of Caloric have been considered. It is sufficient at present to remark, that whatever may be the nature of this power, its existence as the cause of certain effects is demonstrated; and these effects, their relations to each other, and the general laws according to which they are produced, may be investigated with sufficient precision, though the nature of the cause may be unknown.

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SECT. I.—*Of the Distribution of Caloric, and the means of measuring Temperature.*

THE state of a body with regard to its power of producing the effects which arise from the operation of caloric, is termed its Temperature. In every body the temperature depends on the quantity of caloric it contains. If at any temperature it contains a certain quantity, the addition of caloric raises its temperature, and its abstraction equally causes a reduction of temperature.

Some estimate may be formed of the temperature from the sensation it excites, but this method of judging is extremely defective. It is necessarily limited with regard to the range of temperature, since, beyond a certain degree, either of heat or cold, there can be no discrimination; and it is also inaccurate, from the sensations being so much in-

fluenced by various circumstances, besides the direct cause by which they are excited.

The mode, therefore, of estimating the temperature of bodies by the expansion produced by the operation of caloric, was a valuable acquisition. On this is founded the construction of the Thermometer,—an instrument of the first importance in all researches on the subject of heat. Sanctorius had observed the great expansion which air undergoes when heated, and it occurred to him that this expansion might afford a measure of the variations of temperature. The instrument he used was a hollow glass ball, with a long cylindrical stem of narrow diameter: when it is placed in a vertical position, the ball being uppermost, as represented fig. 20, a portion of the air of the ball may be expelled by heat, and the open end of the stem being immersed in a liquid, the liquid rises in the stem when the ball cools, and afterwards, by its ascent or descent, as it is pressed on by the air in the ball expanded by heat or contracted by cold, shews the alterations of volume which the air suffers from these changes of temperature. This instrument is capable of indicating very minute changes of temperature, air being so expansible as to suffer a sensible change of volume, from the slightest variation of heat or cold. It is otherwise very imperfect, being capable of measuring a very limited range of temperature, and being liable to be affected by variations from the atmospheric pressure. Its form is improved by using a ball with an upright cylindrical stem, curved at the bottom as represented fig. 21. It has also been rendered more perfect, and capable of being applied with much advantage to certain forms of experiment, by an invention of Mr Leslie, in which two air thermometers are joined together, so as to

form a curved tube, with a ball at each extremity, represented fig. 17. The elasticity of the air in one ball exactly counterbalances that of the air in the other, and the column of coloured liquid between them remains in equilibrium. But when one ball receives heat, the air inclosed in it being expanded, presses more forcibly on this liquid, causes it to descend in the stem connected with this ball, and to rise in the other. This is named the Differential Air Thermometer.

The thermometer was rendered more manageable, and capable of more extensive application, by substituting a liquid as the measure of expansion, and inclosing it in a tube hermetically sealed. Spirit of wine coloured, and quick-silver, are the liquids usually employed; the latter is the most accurate, as its expansions correspond most accurately with increments of temperature, and being less volatile, it can also measure much higher temperatures: the former has the advantage of indicating lower temperatures, as it does not congeal even at very intense colds. The instrument with either is a glass ball, from which a cylindrical stem of a very narrow diameter issues. The ball is filled with the liquid, and so much more is introduced, that it shall stand at a certain height in the stem, the open extremity of which is afterwards closed. If the ball of the instrument be placed in contact with a hot body, it receives caloric, the liquid within is expanded, and rises in the stem, the rise continuing until the thermometrical liquid attain the temperature of the matter around it. When in contact with a cold body, caloric is abstracted from it; the liquid contracts and descends in the stem; and by a scale of equal parts attached to the stem, the rise and fall of the liquid, and the precise point at which it

stands, which indicates of course its temperature, are ascertained; and from the law that caloric uniformly diffuses itself over bodies, until a common temperature is established, this indicates the temperature of the matter in contact with the ball of the thermometer.

A difficulty was experienced in the construction of the scale, that of rendering it uniform, so that the degrees on one instrument should correspond with those on another. This was remedied by the discovery of certain fixed points in the scale of temperature always the same, and from which the scale may be formed. The points usually taken are those at which water freezes, and at which it boils. If the thermometer be immersed in freezing water, or rather in melting snow or ice, the liquid will stand at a particular part in the stem. If it be plunged in water boiling under a mean barometrical pressure, it will rise and become stationary at another part; and however these experiments be diversified, the liquid will always be stationary at these points. Now, it is obvious, that the space between them may be divided into any number of degrees; and if the instrument is graduated in this manner, the degrees in every thermometer, if the same number be observed, will always be the same; and the scale also may be prolonged in each by similar degrees below the freezing point of water, so as to denote low temperatures, and above its boiling point to express higher temperatures.

The scale thus constructed being arbitrary, different forms of it have been introduced. In this country the scale of Fahrenheit, a German artist, is used. The space between the freezing and boiling points of water he divided into 180 degrees; but instead of commencing the numeration of its degrees at the lower point, the freezing



of water, he began it still lower in the scale of temperature, or at that degree of cold which is obtained from a mixture of snow or salt. The space between this and the freezing point of water, when divided into degrees, such as those between the freezing and the boiling points, gives 32 degrees; the freezing point of water, therefore, is on this scale marked 32, and the boiling point is 180 higher, or 212°.

The scale of Beaumur is rather more simple. It commences at the freezing point of water, which is therefore marked 0, or, as it is named, zero. The space between this and the boiling point of water is divided into 80 degrees; the latter therefore is marked the 80th degree. More lately a similar scale, formerly in use in Sweden, under the name of the scale of Celsius, has been introduced in France: the space between the freezing and boiling of water being divided into 100 degrees, it is hence named the Centigrade scale. This last is perhaps the more natural division, and hence some of the chemists of this country have been disposed to adopt it. Fahrenheit's scale, however, arbitrary as it is in its construction, has two very important advantages: its degrees are much smaller than those of the others, and observations with it are therefore more minute; and the commencement of its numeration being low, there is seldom any necessity of expressing degrees below this: we avoid therefore the ambiguity of negative degrees. If a new scale were attempted, we might find one perhaps uniting every advantage in taking the freezing and boiling points of quicksilver, the usual thermometrical liquid, as those from which the degrees are to be numbered, dividing the space between them into 1000 degrees. The division would thus be

more simple than that of Fahrenheit: the degrees would be still smaller, without being too much so for observation; the commencement of the numeration would be lower, and would correspond nearly with the lowest natural temperature. And although the scale was constructed in relation to these points, the actual graduation of the thermometer might be executed in the usual manner, from the freezing and boiling points of water, it being only necessary to determine carefully with what numbers on the new scale these points correspond.

Two standard points being fixed in all these scales, it is easy to establish their correspondence. Each degree of Fahrenheit's is equal to  $\frac{4}{9}$ ths of a degree of Reaumur's. If, therefore, the number of degrees of Fahrenheit's, either above or below the freezing point of water, be multiplied by 4 and divided by 9, the quotient will be the corresponding number in Reaumur's scale. To bring those of Reaumur's to Fahrenheit's, they must be multiplied by 9, and divided by 4, the quotient gives the number of degrees of Fahrenheit either above or below the freezing point. Each degree of Fahrenheit's scale is equal to  $\frac{5}{9}$ ths of a degree of the centigrade scale: to find the correspondence, therefore, these numbers are to be used as in the above formula.

In employing expansion as a measure of temperature, one very essential point is to be determined, before the accuracy of the method can be admitted: it is whether the expansion and contraction correspond exactly with real increments and decrements of temperature. If a thermometric liquid, from a given augmentation of temperature, say 10 degrees, expand more at one part of the scale than at another, then the indications from its changes of volume

cannot be accurate. This subject has often engaged the attention of chemists, and the result of their researches is, that the different thermometrical liquids do not expand uniformly as the temperature rises, but in an increasing ratio, or from a given increment of temperature they suffer a greater expansion at a high than at a low part of the scale of heat. The expansions of quicksilver are most regular, and hence it gives the most accurate indications. Even these are not perfectly so, but exceed progressively, as the temperature rises, the real temperatures. To render the thermometer, therefore, perfectly accurate, the degrees on its scale ought to be accommodated to the progressive expansion; but there is still some degree of uncertainty as to the amount of the error, and from the mode in which the scale is graduated, its extent is less important; as the two extreme points, the freezing and boiling of water, are accurately fixed, and the amount of the error, from the progressive expansion between these, is divided among the intermediate degrees. It is greatest, therefore, at the mean degree; there it is equal, according to De Luc, to 3 degrees of Fahrenheit; according to Crawford, to not more than one degree.

To measure very high temperatures, other methods must be employed. An ingenious one was proposed by Newton, that of observing the times of cooling in a body which has been at a high heat, until the temperature to which it falls can be ascertained by a thermometer, and inferring what the temperature must have been from the assumption that the times being taken in arithmetical progression, the decrements of temperature are in geometrical progression. Various methods, too, of applying the expansions of solids to this purpose, have been contrived,

furnishing different pyrometers. But the mode which has been regarded as most practicable and accurate is that afforded by the pyrometer of Wedgwood. This is founded on a singular property belonging to clay, that it contracts instead of expanding by heat, the contraction remaining permanent when the heat is withdrawn. To apply this, a gage is employed, formed of two straight rods of brass, 24 inches long, divided so as to form a scale into inches, subdivided into tenths, and fixed on a brass plate so as to converge, the distance between them being five-tenths of an inch at one extremity, and three-tenths at the other. A small cylinder of clay is framed, so that after it has been baked by a moderate heat, it enters the wide end of the groove: when it is exposed to an intense heat, it is contracted in volume, and of course enters farther; and the degree of contraction, and consequently the degree of heat, can thus be estimated by the scale. The commencement of this scale is at the point of ignition visible in day light; which corresponds, according to Mr Wedgwood's estimate, with  $1077\frac{1}{2}$  of Fahrenheit; and each degree of the scale he considers as equal to 130 degrees of Fahrenheit's. There is reason to doubt if this pyrometer is accurate: it is not ascertained if the contractions of the clay are equable, and any error from this source is not guarded against by the graduation being made from certain fixed points. It is useful, however, in giving certain stages of temperature, marked by peculiar effects.

Since the employment of the thermometer, or rather of the expansion of bodies as a measure of their temperature, more just and enlarged views have been acquired of the distribution of caloric. While the property of exciting the sensation of heat was the only one by which that

power was characterized, it seemed a just conclusion, that those bodies which did not excite that sensation contained none of it; an opinion, the fallacy of which is now easily demonstrated.

That the sensation which bodies excite is no just indication of the quantity of caloric they contain, is evident from this, that the power of exciting the sensation depends merely on the relative temperature of the body applied, and of the sentient organs. When the former is at a higher temperature, it gives caloric to the part to which it is applied, and this excites the sensation of heat: when of a lower temperature, it abstracts caloric, and this gives rise to the sensation of cold. Sensations, however, are influenced by preceding impressions. Our body is surrounded with an air, at a temperature generally inferior to the animal temperature, which is therefore always abstracting caloric. Hence it happens, that if any substance is applied to the body inferior to its temperature, but superior to the temperature of the surrounding atmosphere, the abstraction of caloric which it produces is inconsiderable, and, compared with the impression which the air makes upon us, it seems positively warm. In general, therefore, it may be affirmed, that whatever communicates caloric produces the sensation of heat, and that whatever abstracts it has an opposite effect; but this abstraction requires to be greater than that made by the surrounding atmosphere, in order to convey to us the sensation of positive cold. Different bodies too, at the same temperature, occasion different sensations, according to the rapidity with which they absorb, or give out caloric. From both circumstances, it is evident, that the sensation excited by a body is no accurate measure of the caloric it contains, and that the sensa-

sation of cold will be excited by any substance whose temperature is inferior to that of the animal body, though that substance may, and actually does contain a large quantity of caloric.

That bodies at such a low temperature contain it, is evident from the fact, that their temperatures can be farther reduced, and their volume diminished, and it is only by the abstraction of caloric from them that these effects can be produced. Even at the most intense colds there is no reason to believe that bodies are near to being deprived of their caloric, since even then their particles must be far from being in actual contact; and it is only by the repulsive power of caloric that these particles are kept asunder. This affords a more extensive view of the distribution of this power. A solid body is to be conceived of as consisting of a number of particles of the same nature, kept at certain distances from each other by its agency or interposition: when a portion of caloric is withdrawn, these particles approach nearer to each other; and hence the diminution of volume that takes place. But any condensation hitherto effected, is far from that in which these particles would be in contact; nor perhaps is such a condensation possible.

It has farther been established, that the fluid and æri-form states of bodies are owing to the presence of caloric: and therefore, as many liquids require to be exposed to the most intense cold in order to freeze them; as there are even some which have not yet been frozen; and as the greater number of the airs have not been brought even to the liquid state, it is evident that the lowest temperature which has been produced is far distant from that point at which caloric would be entirely abstracted.

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## SECT. II.—*Of the Effects of Caloric.*

CALORIC, by the repulsive agency it exerts, separates the particles of bodies from each other, and this operation, in progressive stages, gives rise to the three general effects of Expansion, Fluidity, and Vaporization. Besides these, when a body is heated to a certain point, it becomes luminous : this state, named Ignition, is an effect apparently unconnected with the others.

### *Of Expansion.*

WHEN the temperature of a body is raised, its volume is enlarged in every dimension ; when the temperature is reduced, it suffers contraction ; and this expansion and contraction are, under a general point of view, proportional in each body to the caloric communicated or abstracted.

The expansion from a given augmentation of temperature is very different in different bodies. Generally speaking, it is greatest in those which are most rare, and which have least cohesion ; hence, it is very considerable in æri-form fluids ; it is less in liquids, and is still less in solids.

In attending to the results more minutely, we find it to be very different in different solids, as for example in the different metals ; and in these differences, little relation is to be discovered between the expansibility and any physical or chemical quality. It has none to the density ; and the only property with which it can be connected is the fusibility ; those which are most fusible suffering the

greatest expansion, though to this also there are exceptions.

In liquids, the degrees of expansion from the same augmentation of temperature are not less dissimilar; and as their expansibility is greater, these differences are even more conspicuous. In general, those liquids that are most volatile are those which are most expansible. Thus, quicksilver in the rise of temperature from  $50^{\circ}$  to  $100^{\circ}$  of Fahrenheit is expanded about  $\frac{1}{170}$  of its original volume, water  $\frac{1}{117}$ , and spirit of wine  $\frac{1}{11}$ .

It might be expected that a similar diversity would exist in the expansions of aerial fluids. Instead of this, it appears to be established, that the expansions of all airs are the same, from the same augmentation of temperature. This has been established by Dalton and Gay-Lussac; the expansion, according to the former, amounting in all of them to  $\frac{1}{117}$  of the volume, for each degree of Fahrenheit; according to the latter,  $\frac{1}{160}$ . The apparent differences which had been observed in preceding experiments appear to have arisen from small but variable quantities of water being present, which, assuming the state of vapour, added to the volume of the æriform fluid.

Another important fact to be illustrated with regard to expansion is, that in many bodies it is progressive with regard to temperature, or becomes greater as the temperature rises. Hence, from a given augmentation of temperature, the expansion is greater at a high than at a low part of the scale of heat.

This is observed particularly in liquids. Dividing the scale of temperature between  $32^{\circ}$  and  $212^{\circ}$  into two equal portions, the expansion in the higher portion, or from  $122^{\circ}$  to  $212^{\circ}$ , is to that in the lower, or from  $32$  to  $122$ , in



quicksilver, as 15 to 14, in oil as 15 to 13, in water saturated with salt as 15 to 11.6, and in alkohol as 15 to 10.9. In all these the expansibility is progressive, though in each to a different extent. The progression becomes more considerable too as the temperature is higher, or rather as it approaches nearer to the boiling point of the liquid.

Since there is this increasing expansion in liquids, it might be expected that it would also be found in aerial fluids. The reverse, however, appears to be the case. The expansion was even observed by Roy and Dalton to be rather a decreasing one, or to become less as the temperature rises. But this apparent result might be owing to the mercurial thermometer not being perfectly accurate, but indicating augmentations of temperature in the higher part of the scale less than the real augmentations; and making allowance for this, according to the correction of De Luc, already stated, the expansions of aerial fluids will be found to be precisely equable.

These apparently anomalous facts, I have endeavoured to connect and explain by the application of the following principle: Expansion is not to be considered as the result merely of the operation of caloric, but as arising from this power prevailing so far over the force of cohesion, which, to a certain degree, always counteracts it where it exists. And considering it under this point of view, these facts may thus be explained.

The inferior expansibility of solids compared with that of liquids, must be referred to cohesion being exerted in the former with greater force than in the latter; and the obstacle to the expansive energy of caloric being therefore more considerable: while the great expansibility of aëri-form substances is owing to there being no cohesion between

their particles : there is therefore no resistance, and enlargement of volume is produced, limited only by the pressure under which the augmentation of temperature acts.

The difference in the expansions of different solids from the same rise of temperature, is evidently to be ascribed to the various degrees of strength with which cohesion is exerted between their particles. The same cause must be assigned for the differences in the expansions of different liquids ; for although in these cohesion is weak, it still exists to a certain extent, different no doubt in each. The equability in the expansions of aerial substances, must, in conformity to this view, be ascribed to the absence of the power of cohesion : there is in all of them no resistance to the operation of caloric, and hence the expansion must be simply in proportion to the rise of temperature, and must in all be the same.

Lastly, the uniformity in the expansions of aerial substances with regard to temperature, while the expansion of liquids is progressive, must be referred to the same cause. In the former, expansion is the effect merely of the operation of caloric, and must therefore be proportional to the augmentation of temperature : in the latter, it is modified by the force of cohesion, which is exerted to a certain extent : the power of this is diminished as the temperature rises ; the resistance therefore to the expansive power is becoming less, and hence the expansions must become greater. It follows from this view, that in solid substances the expansibility ought likewise to be progressive with regard to temperature. The fact on this point is not well ascertained, though there are some observations which appear to prove that it is so. And as the force of cohesion is so great in solids, an elevation of temperature, even to a con-

considerable extent, can have less effect in weakening it: hence the progression may be so inconsiderable, that in the small portion of the scale that can be accurately measured, it may not be easily ascertained.

There remain to be stated some exceptions to the law, that expansion is produced by the communication of caloric.

A striking exception is in the enlargement of volume that accompanies the transition of bodies from the liquid to the solid form. This transition is occasioned by reduction of temperature: it ought therefore to be attended with diminution of volume, or, if no difference can be discovered between the temperature of the liquid, and that of the solid formed from it at the moment of formation, there ought at least to be no expansion. The expansion, with regard to a number of substances, is however very considerable. Water in freezing expands so much as to raise a considerable weight, or even to burst metallic vessels in which it is confined. This has been supposed to arise from the disengagement by freezing of the portion of air which water holds loosely dissolved; but it takes place when this air has previously been abstracted as much as possible, by the action of the air pump. It probably depends, according to the hypothesis suggested by Mairan, on a polarity in the particles of the water, or a disposition to unite by certain sides in preference to others. It is accordingly observed, that the spiculae of ice shoot out at a certain angle; and in consequence of this arrangement an enlargement of volume may be produced. The same phenomenon is displayed by some other substances in their congelation, though not to the same extent; as by several saline solutions, sulphur, and among the metals by iron, bismuth and antimony, and it is no doubt to be referred to a similar cause.

A singular phenomenon, however, peculiar, as far as has been discovered, to water, is expansion, not only in the actual process of congelation, but for several degrees previous to the point at which the congelation commences, and of course while perfect fluidity remains. If water be cooled in a tube adapted to render sensible its changes of volume, it contracts as the temperature is reduced, until it has fallen to about 40 of Fahrenheit's scale; it then becomes stationary: if cooled farther it expands, and continues to expand in an increasing ratio until it freeze. If, by avoiding agitation, the freezing be prevented at the usual temperature of  $32^{\circ}$ , and the water be cooled lower than this, the expansion continues to proceed; it has been cooled down to 20, and even to 10, and at the last temperature it had expanded as much as it would have done had the temperature been raised to 75. The same property is displayed when the freezing point of the water has been lowered, by dissolving certain salts in it; and in this case the expansion commences at about the same distance from the point at which such a solution freezes, as it does from the usual freezing point of pure water.

This property of water, with regard to expansion, had been observed at an early period; and Hooke suggested that it might be not a real, but only an apparent anomaly, depending on the contraction of the containing vessel. The same explanation was given by Mr Dalton. The expansion of water being in an increasing ratio with regard to temperature, the contractions it suffers in cooling must always be becoming less as the temperature falls. They become at length inferior to the contraction of the containing vessel; whence apparent expansion will take place, and for the same reason this will appear to proceed in an

increasing ratio as the temperature falls. It has been found, what appears to be in conformity to this view, that the apparent expansion commences at different points of the thermometrical scale, when the experiment is made in tubes of different kinds, appearing, for example, at a higher part of the scale in a metallic tube and ball, than in one of glass, the contraction which the metal suffers from reduction of temperature being greater than that of the glass.

The reality of this property in water has been established, however, by Dr Hope, by a series of experiments executed in a manner in which this source of fallacy can have no effect: Thermometers being placed near the bottom and top of a cylindrical jar containing water, he observed, that in cooling water until it arrived at  $40^{\circ}$ , the under thermometer always indicated the lower temperature; but in cooling it below  $40$ , the reverse took place, the thermometer at the surface indicating the lower temperature,—a decisive proof, that in cooling below this point water expands, becomes therefore lighter, and ascends. Or, in reversing the experiment, by communicating heat to water which had been cooled down to  $32$ , the thermometer at the bottom was always higher in temperature than that towards the surface; the water as it became heated contracting and falling down. This continued until the temperature rose to  $38^{\circ}$ , then the arrangement was reversed, and the warmer water above this appeared at the surface. It is obvious that these experiments are liable to no fallacy from the contraction or expansion of the containing vessel; since, whatever this be, it must have operated equally on the whole column of water, and they fully establish the existence of this peculiar anomaly in water.

Can any cause be assigned for this peculiarity? Blagden suggested, that that polarity, or peculiar exertion of the attraction of cohesion which unites the particles of water in a determinate manner in congelation, may begin to operate some degrees above the point at which the actual solidification takes place, and give rise to enlargement of volume. There is reason to believe that this even happens with regard to some other substances which expand in becoming solid. Thus, if pieces of solid iron are thrown into melted iron, they at first float, from the greater density of the iron in the liquid state; but in proportion as they melt, they sink, probably from the temperature of the liquid iron being reduced by their fusion, and from this reduction being accompanied with expansion.

There is one other exception to the law that bodies are expanded by the action of caloric; it is that exhibited by clay and the pure earth, argil, which is its base, which, when heated above ignition, contracts instead of expanding as the temperature is raised, the contraction remaining permanent when the temperature is reduced. This might be supposed to depend on the dissipation of volatile matter; but the reverse of this is established by the circumstance, that beyond a certain heat there is no loss of weight, though the contraction continues to proceed far beyond this. It is probably owing to the exertion of the attraction of cohesion being favoured by the high temperature, in consequence of which, the particles composing the mass enter into closer aggregation; and accordingly, what is in conformity to this view, a degree of hardness is acquired, greater as the heat has been more intense. Sir James Hall observed, that a similar contraction takes place

in chalk heated under compression, and this is accompanied with increase of hardness.

### *Of Fluidity.*

WHEN a solid substance is heated to a certain temperature, the force of cohesion between its particles is so far diminished, or is so peculiarly modified, that its parts are moved easily with regard to each other, or it passes into the fluid form. By a reduction of temperature, the particles are again united so as to be subversive of this mobility, or the body returns to the solid state. These changes of form, therefore, may be regarded as depending on the relative action of caloric, and of the force of cohesion. Were cohesion only exerted, the particles of all bodies would be closely united, and all would exist in the state of greatest density and solidity. But this is counteracted by the repulsive agency of caloric, which, when in sufficient intensity, counteracts or modifies the cohesive attraction so far as to produce fluidity.

This effect does not depend, as has often been assumed, merely on the force of cohesion being weakened, but rather on its action being so far modified, as to give rise to a different arrangement of the particles in fluidity, from that which prevails in the solid state. Cohesion remains in the fluid, and it is not easy to determine to what extent; for the mobility characteristic of fluidity may be accounted for on the supposition, that the mutual action of its particles is equal in every direction at the same distance, though a strong force of cohesion may be exerted between them. And that a peculiar arrangement of the particles does take place in the transition of form, is proved by the facts, with regard to the expansion bodies

suffer in becoming solid,—facts inconsistent with the supposition that fluidity depends merely on a diminution in the power of cohesion. This peculiar arrangement, however, depends on the operation of caloric separating the particles to certain distances, and allowing these modifications in their mutual actions to be established. Fluidity is therefore strictly and invariably the result of the exertion of this power, and no body can be said to be more naturally liquid or solid than another. In common language, indeed, those bodies which are liquid at moderate natural temperatures, are said to be frozen or congealed when they become solid, and those which are usually solid are said to be melted when they have been rendered liquid, implying some distinction between these two classes. But this distinction is merely relative, and depends on the different temperatures at which, from the different degrees of force with which cohesion is exerted, these states are assumed.

Though every substance would undergo the change of fluidity from the action of heat, it often happens, with regard to compound substances, that they are decomposed at a lower temperature than that which is necessary to melt them. But if this decomposition be prevented, they may be fused. This is well exemplified in the fusion of chalk or limestone, by heat applied under such a compression, as prevents the dissipation of the aerial matter which enters into the composition of these substances: and in this case, the aerial ingredient seems to share its facility of being acted on by caloric with the solid ingredient, and to communicate to it greater fusibility.

Fluidity differs from expansion in the circumstance that, it is not progressive, but takes place suddenly, and as a



precise temperature: the solid even at one degree lower than its melting point having no appearance denoting approaching liquefaction; and the liquid at as small a distance from its freezing point retaining apparently unimpaired its characteristic mobility. This, however, is not universal, there being some substances which pass through an intermediate stage of softness and viscosity, of which we can even mark numerous shades.

The process of congelation is influenced by certain circumstances besides the reduction of temperature. If agitation be avoided, a liquid may be cooled a number of degrees below the temperature at which it usually becomes solid, without congealing; water, for example, can thus be cooled easily to  $28^{\circ}$ , or  $25^{\circ}$ ; it has been cooled even to  $15^{\circ}$  or  $10^{\circ}$ ; but the moment it is agitated when thus cooled, congelation takes place, and the temperature rises to the usual freezing point. The kind of agitation which has this effect, is rather that which produces a vibration among the particles of the liquid than that which moves the whole mass. Another circumstance, which has an important influence on congelation, is the presence of loose particles of solid matter, and especially of the same kind of matter with that which is to be congealed: thus the introduction of the smallest particle of ice into water cooled, even a little below  $32^{\circ}$ , causes it instantly to freeze.

The influence of these circumstances is to be explained by considering congelation as a species of crystallization arising from the particles of the liquid uniting in a determinate manner. Mere reduction of temperature causes the particles of the liquid to approach in that direction least favourable to the exertion of that modified attraction by which they are to be united in the solid. Agitation,

by the various motions it impresses on the particles, places some of them in that direction in which they are more disposed to unite; and a solid particle, or rather a small solid mass, affords a surface whence attraction can be exerted with more effect, and which, when it does commence, will proceed rapidly through the whole.

During liquefaction, a quantity of caloric is absorbed without producing elevation of temperature,—an important phenomenon more strictly connected with another part of the history of caloric, and which is therefore to be afterwards considered.

#### *Of Vaporization.*

THE term Vaporization is applied to denote that change in which a body passes into the form of vapour or air. It is the immediate effect of the action of caloric. The expansive energy of this power, acting on a solid or liquid, separates the particles to greater distances, until the force of cohesion progressively weakened is entirely overcome, and a repulsion is established between the particles. These receding from each other, the body becomes extremely rare, and highly elastic, and thus passes into what is named the Aëriform or Gaseous State.

In general, bodies pass into this state from the liquid form, and there is often a considerable range of temperature between the two stages at which these changes of form happen. In some cases, however, solids pass into the state of vapour without becoming previously liquid, though if their vaporization be prevented by pressure they suffer liquefaction.

Elasticity, or the capability of being reduced by pressure into a smaller volume, and of expanding when that pres-

sure is removed, is the distinguishing property of bodies existing in this state. They all possess it in a high degree. A moderate compression sensibly reduces their volume; an abstraction of external pressure is followed by a great degree of expansion. This elasticity, too, is much increased by the farther operation of caloric; hence moderate changes of temperature in the aëriform fluids are accompanied with considerable changes of volume, and under high temperatures they become mechanical agents of great power, from the elastic force they exert.

Rarity is another property characteristic of this form. The particles are separated to such distances, that the portion of gravitating matter in a given volume is comparatively small. So few rays of light, too, are reflected, that no impression is made on the organ of vision; hence bodies in this state are invisible, except in the example of one or two elastic fluids, which are distinguished by peculiar colour, or where, as in the atmosphere, from the largeness of the mass, some tint of colour is displayed. The vapours in condensing lose their transparency, from the union of their particles into minute globules. A law with regard to the density of aërial fluids, in relation to the volatility of the substances of which they are formed in their liquid or solid state, has been pointed out by T. Saussure, —that the density is in the direct ratio of the volatility, the vapour of ether, for example, being more dense than that of alkohol, though the ether is more volatile, and the vapour of alkohol being more dense than that of water, though the alkohol is more volatile than the water.

The temperature at which different bodies suffer this change of form is extremely various. Some require a temperature comparatively high, and hence usually exist

in the liquid or solid state. Of these some require even an intense heat: these are named Fixed, in contradistinction to those which are more easily converted into vapour, and which are hence denominated Volatile. There are still others which pass into this form at temperatures so low, that even the greatest cold which we can apply is insufficient to condense them into the liquid form.

Substances which assume the elastic form at temperatures so low as this, being incondensable by the methods we can employ, are considered as permanently elastic. In the language of modern chemistry, they are named Airs or Gases,—these two terms, strictly speaking, being synonymous, though the term Air is also sometimes used not in a generic sense, but is applied specifically to that elastic fluid which forms the atmosphere. Substances, again, which exist in the elastic form, but which, requiring a high temperature to maintain their elasticity, can be easily condensed, are named Vapours. The state in which each exists is precisely the same, and the distinction is only relative, referring to the temperature at which it is assumed.

A different view has sometimes, however, been taken of this subject. The aëriform state has been considered as natural or essential to some bodies; and when this opinion was exploded, and the principle established, that this state uniformly depends on the action of caloric, still it was supposed that in the gases, or those possessed of permanent elasticity, the combination of caloric is more intimate than in the vapours which are more easily condensed. There are no grounds for this opinion. The difference obviously depends on the temperature at which the state is produced. If a body require a high temperature to become elastic, it will of course remain so only while that tempe-

ture is kept up; and when this is reduced, it will return to the liquid or solid form. But, if the elastic state is assumed at a temperature lower than any natural one, or than what can be reached by artificial arrangements, the body will appear permanently elastic as it occurs in nature; and if disengaged from combinations in which it exists, it will instantly assume that state, and will not be obtained insulated in any other. If water, instead of requiring a temperature of  $212^{\circ}$  to convert it into vapour, suffered that change at  $200^{\circ}$  below  $0$  of Fahrenheit, it would always have appeared to us as a permanently elastic fluid, and perfectly analogous, so far as regards its mechanical properties, to atmospheric air.

That this property of permanent elasticity is merely relative, is well established by the condensation of several of the gases, as they have usually been considered, having been effected by the application of intense cold, aided by strong pressure.

On these views is established the chemical nomenclature of the permanently elastic fluids. Being regarded as composed of solid or gravitating matter existing in this form, the generic term Gas is applied to denote the form itself, and a peculiar name is assigned to the solid base of each. Thus, there is one elastic fluid named Oxygen Gas: this phrase is applied to it as it exists in the aerial form, and the term Oxygen is appropriated to its gravitating matter. This matter cannot be obtained solid in an insulated state, owing to the peculiar relation it has to caloric, but it exists concrete in many combinations, and it is only when disengaged that it assumes the elastic form. The affinities of oxygen gas and its specific properties are of course con-

sidered as depending on this base. The same nomenclature is applied to all the permanently elastic fluids.

The transition of bodies into the state of vapour is much influenced by mechanical pressure, which, resisting expansion, counteracts that enlargement of the distance between the particles at which cohesive attraction ceases to be exerted. Hence the variations in the boiling point of liquids, according to the pressure under which heat is applied to them. Water, under the usual atmospheric pressure, boils at  $212^{\circ}$ ; when that pressure is withdrawn to a great extent, it boils at  $180^{\circ}$ : if, on the contrary, it be heated under increased pressure, its temperature may be much elevated; in a metallic vessel it has been heated even to  $400^{\circ}$ , and has still remained in the liquid form. Hence too, under an entire absence of pressure, every liquid evaporates, the quantity being less as it is less volatile. Even quicksilver, which is one of the least volatile, there is reason to believe passes into vapour in the Torricellian vacuum:

The transition into vapour is dependent thus ultimately on temperature, but it is also influenced by pressure; and in those cases where a high temperature is required, the change is not limited to one point, but takes place more or less considerably through a considerable range, less being formed as the temperature is low, and less too as the pressure is greater. Hence the quantity of vapour which rises from a liquid is very variable under these circumstances. Mr Dalton, from an experimental investigation, found, that the vapour rising from water, and remaining in contact with it at the temperature of  $212^{\circ}$ , sustains a column of mercury 30 inches in height, or, under these circumstances, such a quantity of vapour is formed as exerts this

force: at  $122^{\circ}$ , or the mean between  $212$  and  $32$ , it sustains a column equal to  $3.5$  inches; and at  $32$  it is equal to  $.02$  inches. He farther investigated the elastic forces of the vapours from other liquids, these of course being greater as the liquid is more volatile; and from these researches he concluded, that "the force of vapour from all liquids is the same at equal distances, above or below the several temperatures at which they boil in the open air;" so that the forces being known with regard to one substance, and the temperatures at which others boil being ascertained, compared with this, the vapour formed from each, measured by its elasticity, may be discovered. More lately he has inferred, that all vapours in contact with their respective liquids, if these are homogeneous, increase in elastic force in geometrical progression to the temperature; the temperature, however, being measured by a scale, divided on the principle, that the expansion of the thermometrical fluid is as the square of the temperature from its freezing point,—a conclusion of course resting on the truth of this assumption. The increased elasticity of steam in contact with the liquid affording it, as the temperature rises, is owing to a larger quantity of liquid passing into that state, and of course under a given pressure, to the steam being more dense at a high than at a low temperature.

The volatility of a body may be repressed by the affinity exerted to it by a fixed substance, even though this affinity is not strong. Thus the boiling point of water is raised by a salt being dissolved in it.

The transition of substances to the state of vapour appears to be considerably influenced by a current of air. If a liquid be heated moderately in a vessel having an imperfect communication with the atmosphere, it evaporates less

speedily, than if freely exposed to the air; or if an elastic fluid is disengaged slowly by chemical action, its free escape is necessary to its full evolution. Gay-Lussac has farther shewn, that a number of bodies, the more volatile metals for example, may be exposed to a high degree of heat in a covered crucible, without vapours escaping by the sides of the cover, while they arise copiously if the cover is removed. This result may be owing in part to the transition of a body into vapour being more prevented by the pressure of its own vapour, than by the pressure of any other elastic fluid, and partly perhaps to the chemical action exerted by the air on the body evaporating.

An absorption of caloric, producing no augmentation of temperature, attends vaporization, as well as liquefaction, —an important general fact, to be afterwards considered.

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From the different tendencies which bodies have to pass into vapour, we are enabled to separate them from each other when they have been combined, or when they become products of chemical action; and peculiar arrangements being requisite for this purpose, constitute several chemical operations relative to vaporization, the consideration of which, with the description of the apparatus in which they are performed, belongs to this section.

When heat is applied to recover a solid substance dissolved in a fluid, without any arrangement being made to collect the fluid, the operation, which is named Evaporation, is performed in shallow vessels, which, presenting an extensive surface, proportioned to the depth of liquor, allow it to be quickly heated, and the vapour to escape with-



out any resistance. These vessels are of glass, earthenware, or metal, according to the nature of the substances operated on, and the degree of heat which is to be applied. In chemical experiments on a small scale, basons of glass, or of Wedgwood's earthen-ware, sometimes also of silver or platina, are used, the heat being applied by the medium of a sand-bath. In pharmacy and the arts, they are more frequently constructed of iron or lead, and the heat is directly applied.

When the object is to obtain the volatile matter by evaporation, it is carried on in close vessels, constructed so as to collect and condense the vapour. This operation is named Distillation. Different kinds of distilling apparatus are employed, adapted to different purposes.

Where the process is conducted on a large scale, as in the distillation of ardent spirits, the common still, made generally of copper, is employed. The construction of this has usually been extremely faulty. Being made of a considerable depth, proportioned to its diameter, a large body of liquor is to be heated, while comparatively a small surface is exposed to the fire, and hence the waste of heat. And the tube issuing from the head of the still, and conveying the vapour into the spiral tube placed in the refrigeratory, being generally narrow, the vapour is retarded, and by its pressure on the liquor opposes the evaporation. In this country the construction of the common still has, within these few years, received great improvements, by the skillful application of the principles which regulate distillation. The height of the still of the new construction is inconsiderable, compared with its diameter, and the tube is so wide that a free escape is allowed to the vapour; the

distillation is thus performed with a rapidity which would formerly have been thought impracticable.

In the greater number of chemical operations, metallic vessels are liable to be acted on, and hence glass or earthen vessels generally require to be employed in distillation. The retort or conical bottle, the neck of which is bent at an angle of about 60 degrees A, adapted to a receiver B, (Fig. 1. Plate 1.) is the most convenient apparatus of this kind. Sometimes it is convenient to have it tubulated with a stopper adapted to the tubulature, as in Fig. 2. A, and to have the distance between it and the receiver increased, so that the latter may be kept sufficiently cool, by an intermediate tube or adopter B. The heat is applied to it by the medium of a water-bath or sand-bath.

In some cases of distillation, the product is not entirely a vapour, which may be condensed, but there is disengaged an elastic fluid, which is incondensable. The receiver having a bent tube issuing from it, represented by C, Fig. 2. is employed in this case; the condensible part of the product is collected in the body of the receiver, and the elastic product issuing through the tube, which terminates in a vessel of water, may be collected in an inverted bottle or jar.

In certain cases, the product designed to be obtained by distillation, is an elastic fluid, not condensible by itself, but capable of being condensed by being transmitted through water. The apparatus invented by Woolfe, Fig. 3. is employed for this purpose. It consists of a series of bottles A, B, C, D, connected with each other by bent tubes, and connected with a retort generally by the medium of an adopter. The first bottle A is designed to collect any condensible part of the product. In the other bottles, water is placed to nearly one-half their height, re-

presented in the figure by the dotted lines, and the tube passing from the one into the other, dips into the water of the bottle into which it is inserted. The gaseous product is thus transmitted through the water, by which its absorption is promoted; and if any portion is not absorbed by the water, it passes off by a bent tube at the end, and may be collected in an inverted jar, in a trough of water. Each of the bottles except the first has a straight tube, which rises to the height of 10 or 12 inches above its insertion into the bottle, and passes so far within it as to dip in the water nearly half an inch. This tube is termed the tube of safety, and the use of it is to guard against that reflux of fluid which might happen from a partial vacuum arising from condensation in any of the bottles; for as the air is expelled at the beginning of the operation, and its place supplied by vapour, which is liable to condense, the consequence of this condensation is, that the water being more pressed on by the atmospheric air without, than by the gas within, passes backwards from one bottle to another, by rising through the tubes, as from D to C and from C to B, and the different portions are mingled together. It is prevented by the tubes of safety, as, when any such partial vacuum happens, the atmospheric air is forced through the small quantity of liquid in which they are immersed, and rising into the bottles, preserves the equilibrium.

Various improvements have been made in this apparatus. One defect in it is, that we cannot have the advantage of the immersion of the tube which comes from the first bottle A into the liquid in the second B; for as it is designed to collect the condensible product, and ought therefore to be without water, it can have no tube of safe-

ty; and hence, if the tube issuing from it dip into the liquid in the second, whenever condensation happens, from the gas ceasing to be produced, the liquor will pass backwards into it. The contrivance that has been used to obviate this, is the tube of safety of Wether, or bent tube with an additional curvature and a spherical ball, represented Fig. 4. as intermediate between the globular receiver A, and the common Woolfe's bottle B, and connecting them. In this is put a small quantity of water, so as to rise, when the pressure without and within is equal, about half way into the ball. If the elasticity is increased in the internal part of the apparatus, during the distillation, by the production of gas, the water is pressed upwards to the funnel at the top; if there is a condensation, it is forced by the atmospheric pressure into the ball, but whenever it has passed the curvature beneath the ball, it is obvious that a portion of air must rise through it, and will pass into the globe or bottle, to the tube of which it is adapted, and preserve the equilibrium. This tube is rather inconvenient in its form, and liable to be broken, and we can employ no great pressure with it. A simpler contrivance, not liable to these inconveniences, is, having merely a spherical ball in the long leg of the common bent tube, of such a size, that when the liquid in which the extremity of the tube dips, rises into it, this extremity will no longer be immersed, but a portion of the air will enter. The form of this is represented in the tube which comes from the bottle B, Fig. 4.

Another imperfection which attends the common Woolfe's apparatus, is the difficulty of adapting the tubes by grinding, so that it is necessary to secure the joinings by lute. I have avoided this, by having a tube fixed or

soldered when the bottle is made, into that orifice into which the long leg of the tube from the preceding bottle is to enter, of such a length that it is immersed in the liquor within the bottle, and the tube which enters it having a very slight curvature at its extremity, the gas which it conveys is propelled forward, rises through the water, and passes into the next bottle; and as there is no difficulty in grinding the tubes into the bottles *from* which they issue, the whole apparatus is easily constructed without the necessity of lute. There is another form of apparatus which has this advantage, in which, instead of bottles, globes are employed, from which a tube issues, straight at the neck, so that it can be fitted by grinding into the neck of the globe into which it enters, but having such a curvature, that the extremity of it dips into the liquid which this globe contains. This, which is the best of these forms of apparatus, is represented Fig. 5.

A liquid obtained by distillation is sometimes not perfectly pure, or it is dilute from the intermixture of water that has been elevated in vapour along with it. By repeating the distillation of it a second or a third time, it is rendered more pure and strong: and the process is then named Rectification, or sometimes Concentration.

When the product of volatilization is a substance which condenses in the solid form, the process is named Sublimation; and as such products are in general easily condensed, a simple apparatus only is required. The alembic with its capital, Fig. 18. Pl. III. is generally used. The alembic A is a conical shaped vessel of glass, in which the materials are put, and exposed to heat in a sand bath, the sublimate condensing in the upper part of it, and forming a crust on its sides. The capital B is adapted to its mouth

to prevent the escape of the vapour ; a small groove or channel runs in the under part, terminating in a tube projecting from it, by which any liquid is collected and prevented from running down or dropping on the sides of the alembic.

A peculiar apparatus is required for operating on aerial fluids, which remains to be described.

The Pneumatic Trough is the principal part of this apparatus. It is a trough, made of wood, lined with lead, generally of an oval form, about 6 inches deep, from 20 to 24 in length, and at the greatest breadth 15 inches ; a moveable shelf being placed in it, at the depth of 2 inches from the edge, in the longest direction, so as to occupy one-half of the breadth, as is represented in Fig. 7. If a glass jar be filled with water, and placed inverted on this shelf, the trough being filled with water to the edge, it is obvious that the mouth of the inverted jar being surrounded with water, the water within it will be sustained by the atmospheric pressure. If, while thus filled, the extremity of a retort, disengaging gas, be placed under it, as represented Fig. 6., or if another inverted jar, containing any air, be turned up, under the mouth of it, advanced a little over the shelf, the elastic fluid rises through the water, displaces it, and is collected in the jar ; and while the mouth of this jar continues surrounded with water, the included air cannot escape, nor will the atmospheric air find access to it. In this way, aëriform fluids can be collected, preserved, and easily submitted to experiment. Some of them, however, are rapidly absorbed by water. These must be received and kept over quicksilver ; and as this fluid is expensive, and inconvenient from its weight, a smaller trough is employed, either hollowed out of marble

or of a solid block of hard wood. This is represented Fig. 8. with an addition which is convenient, — a small rod fixed in the wooden standard on which the trough is placed, which, by a ring attached to it by a sliding arm, serves to support, without any risk, the jar filled with quicksilver, and placed on the shelf.

The other principal part of the apparatus, for operating on the gases, is the Gazometer, designed to contain gases, so that measured quantities can be withdrawn. One of the most simple forms of it, and which answers sufficiently for all common experiments, is that represented Fig. 15. It is made of tinned iron, the surfaces of which are japanned, and consists of two principal parts; a vessel A, somewhat bell-shaped, which is designed to contain the gas, and a cylindrical vessel of rather greater depth, B, in which the former is placed, and which is designed to contain the water by which the gas is confined. To diminish, however, the quantity of water, this cylindrical vessel has a cone within it, also of japanned tinned iron, C, adapted to the shape of the gas-holder, so that this latter, when pushed down, slides between this and the cylindrical vessel, and a small quantity of water fills up the space between them. The vessel designed to contain the gas, is suspended by cords hung over pulleys, to which weights are attached, so as to counterpoise it. From a stop-cock at the under part of the apparatus, D, there runs a tube under the cylinder, which rises and passes through the cone, the opening by which it passes being soldered so as to be airtight: it terminates by an open mouth at the upper part of the bell-shaped vessel A. This tube, at the part where it is bent at right angles, to ascend as has been described, is connected with another which also runs under the bot-

tom, and ascends on the outside, terminating in the stop-cock E, so that from the one stop-cock to the other, through the gas-holder, there is an uninterrupted passage. When the instrument is to be used, the stop-cock E is opened, and the vessel A pressed down, a sufficient quantity of water being in the outer cylinder; the air of the vessel is forced out by the pressure, and its place is occupied by the water in which it is thus immersed. When this is effected, the stop-cock is closed, and now, if we wish to introduce any gas into the apparatus, a bent funnel, the mouth of which is placed in a vessel of water, is attached to the tube of the stop-cock D, as represented in the figure, and the stop-cock is opened. If the extremity of a retort, or of a tube conveying gas, as represented in the figure, terminate below the orifice of the funnel, the gas will rise along the tube, will ascend to the top of the gas-holder, and this being counterpoised, will, as the gas enters, rise in the water, until it is filled, a quantity of water remaining around the mouth of it, by which the air is confined. When the gas is to be expelled, the stop-cock at D is closed, that at E is opened, a flexible tube is adapted to it, and the gas-holder being pressed down, either by the hand, or by its own weight from the removal of the counterpoising weights, a stream of gas issues from the extremity of the flexible tube, and may be transferred into a jar, or be applied to any other purpose, and its quantity may be measured by the instrument being graduated by a scale marked on the brass rod F.

The instrument connected with the gazometer in the plate, Fig. 16. is a convenient one for procuring gases from any solid substance, by the application of a strong heat. It is an iron bottle A, into which is fitted, by grinding, a



tube bent at an acute angle. To this a smaller tube, is adapted, the extremity of which can be adjusted to various heights, by a circular joint in the middle of it, at *b*. The bottle containing the materials from which the elastic fluid is to be disengaged, is placed in a furnace, or in a common fire, so as to be raised to a sufficient heat; the gas issues at the extremity, and may be conveyed into the gazoneter, or received in an inverted jar on the shelf of the pneumatic trough. At the end of the operation, the gas ceasing to be produced, as the heat diminished, the water would be pressed into the tube, and might rise into the bottle, if the joinings were not opened. The easiest way of obviating this, is by having a small stop-cock in the tube, as at *c*, which may be opened when the production of the gas has ceased.

When a gas is extricated, in consequence of chemical action, with the application only of a moderate heat, the flask or cucurbit, with a bent tube ground to it, Fig. 19, is the most convenient.

In all accurate experiments on gases, it is of importance that the quantities should be determined with precision; and as to weigh the gases requires a very delicate and complicated apparatus; and is troublesome in the execution; chemists measure them by their volumes, and find their weights by a reference to the tables of their specific gravities which have been constructed. Hence jars graduated into cubic inches and tenths are convenient, as are also, in other cases, jars graduated into equal arbitrary parts, as represented Fig. 23. In thus estimating the weights of gases from their volumes, several circumstances require to be attended to, particularly the temperature and the pressure. Elastic fluids being so expansible, it is ob-

vious that a considerable change in their specific gravity will be made, by a trivial alteration of temperature; the volumes therefore are always reduced to the standard temperature of 54.5, at which their specific gravities are ascertained. It is also necessary to attend to the varying pressure, whether of the atmosphere, or of any fluid in which the vessel containing the gas may be placed. The weight of the gases is fixed at the mean barometrical pressure 29.85 inches of mercury; and if the atmospheric pressure vary from this, the correction by which it is reduced to the standard is to multiply the real pressure, under which the gas is, by the volume of the gas, divide the product by the mean barometrical pressure, and the quotient is the volume under that pressure. The effect of the pressure of the fluid surrounding the jar is most easily obviated, by bringing it, where this can be done, to the same height without and within, or if not, making the necessary correction according to its height and specific gravity.

#### *Of Ignition.*

THE effects arising from the operation of Caloric, hitherto considered,—Expansion, Fluidity and Vaporization, may be regarded as different degrees of one more general effect,—the increase which it occasions in the distances of the particles of bodies. Ignition, or Incandescence, cannot be referred to this cause, and it has apparently no connection with the others.

By Ignition is meant that illumination or emission of light, produced in bodies by exposing them to heat, and which is not accompanied by any other chemical change. It is distinguished from combustion, in which there is also the emission of light and heat, by being the effect of the

high temperature alone; while combustion is a process depending on the action of the air, of which certain substances only are susceptible, and which, when the process has ceased, cannot be renewed in the residual matter. Ignition is independent of the air; all bodies, at least all solid and liquid substances, are susceptible of it; and if it has ceased from a reduction of temperature, it may be renewed by the temperature being raised.

Ignition appears to take place in all bodies at the same temperature. This is not far distant from  $700^{\circ}$  of Fahrenheit. Quicksilver boils at a temperature corresponding with  $672^{\circ}$  of Fahrenheit, and it, even when observed in the dark, does not while boiling appear luminous. Dr Irvine, from the heat which iron communicates to water, endeavoured to determine the temperature; the heat of a common fire he found to be about  $790^{\circ}$ ; hence, the commencement of ignition must be between this and the boiling point of quicksilver. Wedgwood had fixed it at  $947^{\circ}$ , by measuring the expansions of silver in a pyrometrical gage: these being probably progressive with regard to temperature, would lead to the fixing it too high.

In the first stage of ignition, the red rays of light only are given out; as the temperature is raised there is an intermixture of others; and at the highest stage of ignition, there is the due proportion which constitutes white light. This continues undiminished as long as the temperature is kept up.

The æriform fluids cannot be brought into a state of ignition, or rather cannot be rendered luminous, for at the due temperature their particles are probably ignited, but from their rarity a sufficient number of rays are not emitted from a given space to produce the sensation of vi-

sion. If a solid body be suspended in air at this temperature, it accordingly is soon rendered luminous.

Ignition is produced by friction and percussion as well as by the communication of heat: a piece of glass, for example, can be rendered red hot by being pressed against a wheel of grit-stone revolving quickly; and the spark struck from a flint by steel is a similar example. The ignition in these cases is probably produced by the high temperature which the attrition or percussion excites.

The theory of the production of ignition remains obscure; for it is not very obvious, how the raising the temperature of bodies should cause them to emit light. It has been supposed that the caloric is converted into light; but we have no proof of the possibility of this conversion; and, if it were possible, no cause is assigned, why it should take place at the temperature of ignition. A more probable opinion is, that the heat, by its repulsive agency, expels the light which the body contains; though with regard to this, also, there is the difficulty of accounting for the emission of light for an unlimited time. Where, however, the ignition is excited by the communication of heat, light is always communicated at the same time; where it is excited by attrition or percussion, it is not proved that the ignited state can be preserved indefinitely; and, if it were, there is the same difficulty in this case with regard to the unlimited evolution of caloric as of light. The subject, however, is involved in difficulties which cannot be elucidated, until the relation between these two powers, at present so obscure, is better known.

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SECT. III.—*Of the Communication and Diffusion of Caloric.*

ALL bodies are permeable to caloric, and its uniform tendency is to diffuse itself over matter, until an equilibrium of temperature is established. If a body, therefore, at a high temperature be placed in the neighbourhood of others at a lower, its excess of caloric passes off from it, until it arrive at the temperature of those around it; or, if a cold body is placed among others that are hot, it receives caloric until its temperature rise to an equality with theirs. This propagation of caloric takes place, even through the most perfect vacuum that can be obtained, and hence is evidently principally owing to its repulsive power; it is also, however, influenced by the nature of the medium in which it takes place, and therefore depends in part likewise on some relation between it and the bodies which receive or part with it.

This diffusion of caloric takes place in two modes. From a heated body a portion of caloric is always communicated to the matter in contact with it, and is diffused through that matter with a certain degree of celerity. But, besides this, a portion is projected from the surface of the heated body in right lines with great velocity, and to considerable distances. The diffusion of caloric, therefore, must be considered under these two modes of radiation, and slow communication.

*Of the Slow Communication of Caloric.*

CALORIC, when communicated by bodies to the matter with which they are in contact, is given out by them with different degrees of celerity, and is received by them with similar differences. There is a similar difference in the celerity with which it is diffused through them. Some, therefore, quickly assume the temperature of the surrounding matter, and allow of this temperature being soon established through their whole mass, while others do so much more slowly.

The property, in consequence of which, bodies thus receive caloric, allow it to be conveyed through their substance, and part with it to others, is named their Conducting power. Those which receive and part with caloric quickly, are those also through which it is diffused most speedily; and they are considered as better conductors than those in which the same effects are more slowly produced. In this property there are great differences, there being scarcely two bodies from or through which caloric is communicated with equal facility.

This property can scarcely be connected with any of the physical qualities of bodies. There is, indeed, a general relation between it and their density; those which are dense, as the metals, being the best conductors; and those which have much rarity, conducting much less perfectly. But in examining more minutely the degrees of conducting power, we do not find that they are proportional to the densities, even among those bodies which have a similar nature, as among the different metals. In substances which are very porous, and in the interstices of which a quantity of air is lodged, the conducting power is very imperfect, which ap-

pears to be owing principally to the air being a bad conductor, and to its motion, by which it might distribute caloric more quickly, being impeded by the force with which it is retained.

It is to this cause, that the imperfect conducting power of fur, flannel, and other similar substances is owing, and on this depends their utility as articles of clothing, in preventing the abstraction of warmth.

To this difference, too, in conducting power, is owing the difference in the sensation either of heat or cold, excited by different bodies applied to our organs of sense, when the thermometer shews their temperature the same. Those which part with caloric most readily will be those which, when applied hot, will give the greatest sensation of heat; and the same bodies, being those which receive caloric most readily, will be those which, when cold, will abstract it most rapidly, and will therefore produce in greatest intensity the sensation of cold.

Many useful applications are made of this difference in conducting power, as in the various arrangements to prevent the waste of heat in chemical operations, or to guard against the effects which arise from sudden alterations of temperature.

The communication of temperature through liquids, is much accelerated by their mobility; the portion directly receiving heat having its density diminished, it must unless it occupy the surface change its place; it is succeeded by another portion heated in its turn, and thus a circulation is established through the whole mass of liquid, by which the increased temperature is sooner established than it would be, were the caloric communicated, as in solids, merely from one particle to another.

Rumford, from some observations on the rapidity of the currents in a liquid while heating or cooling, and on the slowness with which it is heated or cooled when these are prevented, advanced the opinion, that it is by these motions that the uniformity of temperature through it is established, and that liquids in themselves are non-conductors of caloric, or are incapable of communicating it from one particle to another. In support of this opinion, he brought forward a series of experiments, placing in a striking light the slowness with which caloric is transmitted through a fluid, when the motions of its mass are impeded. He also endeavoured to establish, what would have demonstrated the truth of his opinion, that increased temperature cannot be communicated from the surface of a liquid, downwards to the rest of the mass. But, in all his experiments, the results are either inconclusive, or require so many assumptions to render them otherwise, that the opinion remained extremely problematical. The principal fact from which the question can be decided, that relating to the communication of temperature through a fluid from its upper surface, has been made the subject of experiment by various chemists, and in all of these the communication has been proved to take place. There is one source of fallacy, indeed, attending the experiment, from the conducting power of the vessel containing the liquid which may convey a portion of caloric, and communicate it to the under portions of the liquid. But, when this is guarded against by various arrangements, or still more effectually by making the experiment at the temperature of  $32^{\circ}$ , and in a vessel of ice, which not being capable of having its temperature raised above that point, is of course incapable of communicating any higher temperature, the same general result is obtained, a result



which sufficiently establishes the conducting power of liquids.

This conducting power, there is reason to believe, however, is not very considerable, since from the mobility of a liquid, a particle of it, when heated, recedes from the others, and yields the caloric it had received less readily; and hence caloric is diffused through liquids, principally by the motions produced by the changes of density they suffer from changes of temperature. Still we can discover in liquids, different degrees of conducting power: thus, quick-silver takes the temperature of any body with which it is in contact, and admits of this temperature being uniformly established through its mass, much more quickly than water or alcohol;—a difference which cannot be ascribed to its being more expansible or more mobile, for neither of these is the fact, and which must therefore be referred to superior conducting power,—a superiority in conformity to the general fact, that metals conduct caloric better than other substances.

A similar opinion was advanced with regard to aerial fluids,—that they also are non-conductors. It rested on observations and experiments still less conclusive than those adduced to establish the non-conducting power of liquids; and the same conclusion that they are only imperfect conductors, is probably to be drawn with regard to them. We can even observe differences in the conducting power of different gases. Thus humid air conducts caloric better than dry air, and hence the greater sensation of cold we experience from it when at a low temperature. Mr Leslie has found, too, that bodies cool with different degrees of celerity in different elastic fluids; and from the phenomena

of this cooling he infers, that this is owing to these having different conducting powers.

It is by the movements of fluids, elastic and non-elastic, that caloric is distributed with more uniformity in nature, and that the temperature of the globe is preserved more equable than it otherwise would be. The atmosphere, when heated at the earth's surface, is expanded, becomes lighter, and recedes from it to the upper regions. An ascending current is thus formed, wherever the earth is much heated, which is replaced by cold air flowing at the surface, and this prevents that progressive augmentation of temperature which would otherwise happen. The warm air is, from the constant ascending current, propelled to colder regions, where it yields its excess of heat. A similar agency, though to a less extent, is exerted by the water of the ocean. When cooled at the surface, it becomes heavier and descends; and, from its saline impregnation, this continues to take place to a lower temperature than if it were fresh. A portion of warmer water of course ascends, and from the great depth of the ocean this circulation continues, communicating warmth, and the water at the surface does not freeze, except in latitudes where the most intense cold prevails. From these movements it is not improbable that there is a general circulation in the ocean, as there is in the atmosphere; the water which has descended in colder regions spreading on the bottom of the sea, flows towards the equator, which must produce a current at the surface in an opposite direction, and thus the heat of the torrid zone may be moderated, as well as the cold of the polar circle.

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*Of the Radiation of Caloric.*

BESIDES the caloric which a body in cooling communicates to the matter with which it is in contact, a portion is thrown from its surface in right lines, moving with great velocity, capable of being rendered sensible at a considerable distance, and obeying the same laws of motion as the rays of light. This forms the radiation of caloric. It was observed more than a century ago, by Mariotte, and also by Lambert; more lately, it has been investigated by Scheele, Saussure and Pictet, Herschel, and Leslie.

The experiment in which this radiation of caloric is best displayed, consists in placing a hot body, as a heated ball of iron, in the focus of a concave metallic mirror, opposite to which, at the distance of 8 or 10 feet, is placed a similar mirror, having the ball of an air thermometer in its focus\*. The moment the hot body is introduced, the opposite thermometer indicates elevation of temperature, the air in its ball being expanded, and pressing on the liquid so as to cause it to descend. If the hot body be withdrawn, or if a screen be interposed between the mirrors, the temperature falls, and the liquid in the thermometer returns to its former height. In this experiment, it is obvious there is projected a calorific matter from the heated body, on the surface of the mirror in the focus of which it is placed; this is reflected in right lines from the surface of this mirror to the one opposed to it, it is again reflected from the surface of that mirror, and is collected in its focus where it produces a heating effect.

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\* The differential air thermometer is well adapted to shew these effects, and to allow the facts with regard to the radiation of caloric to be determined with much accuracy. It was invented and applied to this purpose by Mr Leslie.

The effect is similar with a single mirror. If a hot body be placed before its concave surface, at the distance of a few feet, and a thermometer be placed in its focus, rays of caloric are projected from the hot body, and are reflected from the surface of the mirror on the thermometer, producing elevation of temperature.

That it is not the contiguity of the hot body to the thermometer that produces the effect in these experiments, is shewn, not only by the distance at which it happens, but by moving the thermometer a little out of the focus, even nigher to the heated surface, when its temperature, if it had been previously raised, immediately falls.

The rise of temperature produced by this radiation is greater, the hotter the body is from which it takes place. In using the apparatus of the double mirrors, and placing in the focus of one of them a ball of iron, two inches in diameter, at an obscure red heat, the rise produced in a thermometer, in the focus of the other mirror, at the distance of 12 feet, is equal to about  $20^{\circ}$  of Fahrenheit's scale. From a glass matrass, containing about two ounces of water boiling, it does not exceed three degrees. From burning charcoal, the heat is such, that it can set fire to a burning body at the distance of several feet.

The velocity with which radiant caloric moves, is not capable of being measured at any distance at which we can make the experiment. In an experiment by Pictet, the effect appeared instantaneous at the distance of 69 feet. It appears to pass through the atmosphere without interruption; nor, according to Scheele's experiments, is its direction changed by a current of air. It is stopped, however, by liquids, even the most transparent.

Glass also intercepts a large portion of it. If a plate of

clear glass be interposed half way between the two mirrors, a hot body being in the focus of the one, and the ball of a thermometer in the focus of the other, the effect on the thermometer is nearly entirely intercepted. The rays of caloric thrown on the glass, instead of passing through it, are absorbed by it. This result affords a method of separating the rays of caloric from the rays of light when they accompany each other. Thus, if a burning candle be placed in the focus of the mirror, and a plate of glass be interposed, a luminous image is formed on the ball of the thermometer in the opposite focus, from the light passing through the glass, but the calorific effect is greatly diminished, by the rays of caloric being arrested,—a fact which shews well the essential difference between radiant caloric and light.

Dr Maycock had shewn, however, that the rays projected from a body considerably heated pass through glass. It also appears, from recent experiments by Dr Delaroche, that the power of radiant caloric to penetrate glass is much dependent on the temperature at which it is projected, the rays emitted from a body at  $212^{\circ}$  being scarcely capable of passing through glass, but acquiring this property if the temperature is raised considerably higher. He farther found, that the rays which have once passed through a plate of glass pass more easily through a second plate. And he farther concludes, that the rays emitted simultaneously from the same heated body differ from each other in the power of penetrating glass.

Some bodies are more disposed to absorb radiant caloric than others, and hence are much more heated by it. Scheele observed, that when a glass mirror is used instead of a metallic one, the heat is not reflected, but is absorbed

and retained by the glass; and the result is similar, if a metallic mirror have its surface blackened. Pictet found, that when the glass bulb of the thermometer is blackened, it is considerably more heated than when it is clean. But if the bulb be covered with tinfoil, the reverse happens, or the elevation of temperature is much less than when the glass bulb is opposed to the mirror.

The power of reflecting the rays of caloric is of course the reverse of the absorbing power. Metals reflect most perfectly, hence the calorific effect is greatest in those experiments when metallic mirrors are employed; it is less with a glass mirror, and is scarcely sensible when the surface is blackened. It is, for the same reason, least when the ball of the thermometer has a metallic surface, is greater when of glass, and still greater when blackened.

An important difference exists among bodies in the power of radiating caloric, the quantity thrown from different kinds of surfaces at the same temperature being very different. For the knowledge of this we are indebted to Mr Leslie. The apparatus he employed to determine it is very simple. It is a canister of tinned iron in the form of a cube, the sides being six or eight inches square; this is filled with hot water, a thermometer being inserted in it, to shew the temperature during the continuance of the experiment. The sides of the canister are variously prepared; one, for example, is blackened, another is covered with paper, a third has a plate of glass applied to it, and the fourth is left clean. When thus prepared, it is placed before the concave surface of a mirror of tinned iron, at the distance of three or four feet; the ball of the differential thermometer being adjusted to the focus. All these surfaces being equally under the influence of the hot wa-

ter in the canister, are at the same temperature, and their comparative powers, in radiating caloric at a given temperature, can be ascertained. In this respect they differ widely; as an average it may be stated, that the calorific effect from the blackened surface being 100, that from the paper is 98, from the glass 90, and from the clean metal not more than 12.

It thus appears, that those surfaces most disposed to absorb radiant caloric, when it is thrown upon them, are those likewise most disposed to radiate it when they are at a high temperature, and the absorbing and radiating property are opposed to the reflecting power.

It is an interesting question on this subject, does radiant caloric suffer refraction? This was attempted to be determined by Pictet, but the experiment was so imperfectly performed, that no conclusion could be drawn from it. Herschel found reason to conclude, that rays of caloric exist in the solar beam, apart from the rays of light, and that these are separated when the beam is decomposed, by being passed through the prism, the calorific rays being thrown beyond the red ray; this, if the experiment were accurate, proved, that these calorific solar rays are subject to refraction. He farther submitted to experiment, the radiant caloric projected from heated bodies; and he found them to be refracted by a lens, and, in the spot where they were collected by the refraction, to produce a heating effect. The refraction of the rays of caloric has farther been proved by the experiments of Berard, who has also shewn that they are polarized by reflection like those of light.

Mr Leslie observed, that a considerable aberration happens in the reflection of heat; hence, when reflected from

a mirror, the maximum of heat is not in the true focus, but is considerably nearer to the surface of the mirror.

The experiments of Herschel establish the important result, that radiant caloric exists in the rays from the sun, and that on this depends their heating power. In decomposing the solar beam by transmission through a triangular glass prism, it is resolved into different coloured rays, and these Herschel found were possessed of different degrees of heating power; the violet ray, which is the most refrangible, and which bounds the coloured spectrum on one side, being least powerful in exciting heat; and the calorific power, increasing towards the other side, bounded by the red ray, which far exceeds the others in heating power.

This might be considered as arising from a diversity of heating power in the visible rays of light; but Herschel farther found, that calorific rays which produce no illumination exist in the solar beam, and being less refrangible than any of the rays of light, occupy a space beyond the red ray, when the entire beam is decomposed by the prism. In this space, to the extent even of half an inch beyond the visible light, the heating power is actually greater than in the space occupied by the red ray, which of any of the coloured rays produces the greatest heat, and it can be traced even to the extent of an inch and a half. This appears to prove the existence of rays of caloric in the solar ray, which, from being less refrangible, are capable of being separated from the visible light, and if the accuracy of the experiments be admitted, scarcely any other conclusion can be drawn. Herschel farther infers, that the heating power of the different coloured rays does not belong to the light of these rays, but depends on rays of caloric asso-



ciated with them, there being, according to his conclusions, rays of caloric as well as of light of different degrees of refrangibility, and the former being therefore spread over the space occupied by the prismatic spectrum as well as the latter. The experiments from which this was inferred will be more fully stated under the history of Light. It is to be remarked, however, that in the more recent experiments of Berard, though the different heating powers of the coloured rays were found to be nearly as Herschel had stated, the maximum of heating power was found to be at that extremity of the spectrum bounded by the red ray, and to be diminished beyond it, so that where there was no visible light the rise of temperature was only one-fifth of what it was in the red ray.

In one respect the calorific solar rays differ from those from heated bodies; they pass with less interruption through transparent media: this is evident from the intense heat produced in the focus of a lens when the rays of the sun have been transmitted through it. It was ascertained, too, with more accuracy by Herschel; the solar calorific rays, whether associated with light or separated from it, passing through transparent substances and producing heat; while the radiant caloric from heated bodies is almost entirely arrested. It has been already stated, that the experiments of Delaroche prove that the rays projected from a hot body penetrate glass, and do so with much more facility when the body is highly heated, than those emitted from a body at a low degree of heat. This accords with the peculiarity of the solar calorific rays, as these, from their high heating power, may be considered as analogous to those projected from a body at a very high temperature.

An important subject of inquiry is still to be consider-

ed; What is the nature of Radiant Caloric, or what theory can be given of the phenomena it displays?

The phenomena appeared to prove the existence of a subtle calorific matter, projected from heated bodies, capable of moving in right lines with velocity, and obeying laws of motion similar to those of light. Mr Leslie advanced a different hypothesis; the apparent calorific emanation he supposed to be propagated by the medium of the air. The heated surface, according to his view, communicates increased temperature to the air in contact with it; this layer of air is expanded, and presses on the portion immediately before it. This is successively, but rapidly renewed; a chain of undulations is propagated from the heated surface to the mirror, is reflected and concentrated in its focus; and each pulsation being accompanied, according to the hypothesis, with a discharge of the caloric by which the expansion exciting it had been produced, the whole is transported with the velocity of these undulations, and the calorific effect is obtained when they are concentrated on a solid substance. The degree of heat excited will be greater as the temperature of the surface communicating it is greater. And the diversity in the effect from different kinds of surface at the same temperature, Mr Leslie supposes to be owing to these surfaces admitting of a more or less perfect contact of the atmospheric air; those with which the air comes into closest contact, which is held to be the case with the blackened surface, communicating the largest quantity of caloric in a given time; and for a similar reason, the same surfaces will be those most disposed to receive caloric, and will therefore be those most heated by this kind of communication.

This explanation rests principally on certain facts observed by Mr Leslie with regard to the effect of skreens in-

terposed between the hot body and the mirror on the calorific radiation. When a plate of glass is interposed, the effect on the thermometer in the focus is greatly diminished. He found that this is much dependent on the distance at which the glass plate is placed from the heated body. With the single reflecting mirror, if the plate of glass be placed at about two inches from the blackened surface of the canister, a rise in the thermometer is produced equal to about one-fifth of what would be produced by the same surface, the glass being withdrawn; if farther removed from the heated surface, the effect diminishes, and when it is removed about a foot, it does not amount to one-thirtieth of what it is in the first position. He farther found, that the effect is very different with skreens of different kinds; thus if a metallic skreen be used, though extremely thin, as for example gold leaf, the effect on the thermometer is completely intercepted.

These results cannot be explained on the supposition that these skreens operate by intercepting more or less the calorific radiation; for, were this the case, the action of those which allow a certain degree of heating effect to be produced on the thermometer ought to be the same at whatever distance it is placed from the heated surface, while it is much dependent on its contiguity to it. They therefore, Mr Leslie conceives, establish the conclusion, that these skreens, in every case, arrest the radiant caloric, and that where any effect is produced on the thermometer, this is to be ascribed to the interposed skreen acquiring heat, and being enabled to display the same action as a similar radiating surface would do at the same temperature. Accordingly, when a skreen is employed which is not disposed to receive radiant caloric on the one hand, or to radiate it

on the other, as one of metal, no effect is produced; or if the skreen is such, that its temperature cannot be raised, as is the case with a plate of ice, there is no effect; but, if the skreen be of a substance disposed both to absorb and radiate caloric, as in the case with glass or paper, then a certain effect will be produced, the side next to the hot body arresting the calorific radiation and having its temperature raised, and the other radiating proportional to this rise of temperature,—and this, of course, will be greater the higher the skreen is to the heated body.

Now this effect of these interposed skreens, Mr Leslie conceives, can only be explained on the supposition that the air is the vehicle of the communication as already explained, the skreen arresting the chain of pulsations, and acquiring in its turn the power of transmitting these pulsations with the accompanying discharges of caloric from the other surface.

The conclusion is one which does not necessarily follow, ~~and~~ it is equally conceivable, on the hypothesis of rays of caloric, that these may be arrested by the skreen, its temperature may be raised, and corresponding rays be projected to a certain extent from its other surface: it must, in fact, be supposed, that the interposed skreen receives caloric at the one surface, and communicates it from the other, whether the caloric be propagated by pulsations in the atmosphere, or by projection of calorific particles; and in either hypothesis, those most disposed to receive it, and to discharge it, will be those which will admit of the greatest heating effect being produced on the thermometer. There is also an obscurity with regard to the principle of Mr Leslie's explanation; for admitting, that a chain of vibrations may be established in an elastic medium from a

heated surface, it is not obvious how each pulsation should be accompanied with a discharge of the heat by which it had been excited. Or if there is any necessary connection between these events, there remains the difficulty of accounting for the slow communication of caloric through elastic fluids. The hypothesis, too, is incompatible with the results of the experiments of Herschel and Englefield, which establish the existence of a solar calorific matter, capable of rapid projectile motion. These experiments, however, Mr Leslie considers as fallacious.

It has sometimes been conceived that radiant caloric is a species of light. Dr Hutton, assuming that the heating powers of the different species of visible light are not proportional to their power of exciting vision, supposed there might be a species of light capable of exciting temperature without exciting this sensation, and such he conceived to be radiant caloric. Such an hypothesis must appear doubtful. So far as we can trace, radiant caloric has all the properties of caloric conveyed by slow communication, and the circumstance of its assuming a state of projectile motion, if it actually do so, is insufficient to identify it with light. It exerts none of the chemical agencies of light. And the very basis of the hypothesis is subverted; for, as is afterwards to be stated, it is uncertain if any of the rays of light apart from caloric have a heating power. Yet the fact already stated, that the radiant caloric projected at a high temperature penetrates transparent media with more facility, shews some approximation to the properties of light, and it is conceivable that a higher degree of the same power might render them capable of penetrating the organ of vision, and exciting the sensation of light.

It is an interesting subject of investigation; What is the relation between the two modes in which caloric is discharged from bodies, that by radiation, and that by slow communication? There appears, in general, reason to infer, that those which at a given temperature give off most caloric by communication, discharge least by radiation, and *vice versa*,—metals, for example, radiating imperfectly, while they yield caloric readily by communication, while glass is, with regard to these properties, the reverse.

An inquiry of equal importance is, What proportion does the caloric discharged by radiation from a body suffering reduction of temperature, bear to that given out by slow communication? The influence of each of these modes is established by numerous facts. That of slow communication is well shewn by the different degrees of celerity with which a body cools, according to the conducting power of the medium with which it is in contact, or according as the conducting power is favoured by frequent renewal of that medium, as, for example, by the application of a current of air, or agitation in a liquid. The influence of radiation is not less important, and has, in particular, been established by some experiments by Mr. Leslie on the celerity of cooling in vessels, which radiate caloric unequally; water, for example, cooling more quickly in a tin vessel coated with lamp-black than when clean, the coating, though diminishing the conducting power, more than compensating for this by increasing the radiating power.

The proportion between the two must be considerably dependent on the temperature at which the estimate is made; for at high temperatures the cooling by slow communication will be accelerated by the more rapid current formed in the surrounding medium from the heated sur-

face, while this can have no effect on the radiation. Mr Leslie concludes from his experiments, that at low temperatures the heat lost by the direct communication is somewhat less, and at higher temperatures considerably greater than what is lost by radiation. According to Delaroche, the quantity of heat given out by a hot body in a given time by radiation to a cold one, at a distance, increases in a greater ratio than the excess of temperature of the first body above the second.

The influence of the circumstances connected with radiation on refrigeration, gives rise to some results rather singular, and to some practical applications of considerable importance. Thus water cools more quickly in a metallic vessel, the outside of which is blackened, coated with varnish, or even covered with linen, than when clean and polished, as these coverings accelerate the radiation. Hence, in conducting the process of artificial refrigeration, vessels with such coatings will allow it to be performed most quickly; for the same reason, where the object is to condense vapour or steam, as, for example, in applying this condensation to procure heat, the external surface of the tubes through which the steam passes ought to be painted or blackened; while, if it is of importance to prevent as much as possible the condensation, as in conveying steam, or applying its elasticity as a mechanical power, the external surface ought to be clean and bright.

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THE law observed by a body in cooling, in whatever mode the caloric be given out from it, whether by radiation or communication, has been frequently a subject of

investigation. The higher the temperature is, a larger quantity of caloric is given out in a given time, and, of course, the nearer a heated body approaches to the temperature of the surrounding medium, smaller portions are evolved. Newton supposed that the progression is geometrical, taking the times in arithmetical progression, and this law appeared to be established by the experiments of Kraft and Richman. Martine inferred that the decrements of temperature in a body cooling are partly equable, and partly in proportion to the subsisting heats; and Mr Leslie has drawn the conclusion from his experiments, that the rate of cooling follows a higher ratio than the difference of temperature.

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A singular phenomenon connected with the radiation of caloric is the apparent radiation of cold. When a cold body, as a mass of ice, is placed in the focus of one of the mirrors, the thermometer in the opposite focus instantly suffers a reduction of temperature, greater as the cold of the body is more intense. The experiment was made at an early period by the Florentine Academicians, but it had not attracted notice until again performed by Pictet. Mr Leslie has since ascertained, that the phenomena, with regard to this apparent radiation of cold, are the same as in the radiation of heat, and the same laws are observed. It is greatest at a given temperature from a blackened surface, rather less from a surface of glass, and much less from one of metal; it is reflected by a metallic surface, from a glass surface the reflection is much less perfect, and, in consequence of this, the frigorific effect is greatest when the bulb of the thermometer is of glass, and especially when



it is blackened, while it is inconsiderable when the bulb is gilt. The comparative powers of different surfaces in radiating, reflecting, and absorbing cold, are thus exactly the same as their powers of radiating, reflecting, and absorbing heat. The effects of interposed skreens too, Mr Leslie found to be similar. A metallic skreen completely arrests the frigorific effect, while one of glass allows it to take place to a certain extent, more or less according to its proximity to the cold body.

Cold being merely the negation of heat, and not arising from the action of any positive power, this result of a frigorific radiation appears at first view extremely singular, and difficult of explanation, in conformity to this principle. The diminution of temperature has been ascribed to the radiation of caloric from the thermometer; and in a general point of view this appears to be just, though there is some difficulty in explaining how the cold body acts in producing this radiation. Prevost supposed that there is a constant interchange of heat between bodies by radiation, the quantity radiated by each being less as the temperature is low; when two bodies, therefore, at different temperatures, are placed, as in the arrangement which constitutes this experiment, one in the focus of each mirror, so as to exclude the action of others, and concentrate that from each, there will be such an interchange of caloric between them according to their temperatures: the thermometer in the focus of the mirror radiates caloric, the cold body in the opposite focus likewise gives off caloric by radiation, but this being less than what is radiated from the thermometer, the latter receives less than it gives out, and its temperature falls. This explanation appears to account for the general result, but it fails in accounting for the effect of dif-

ferent surfaces in radiating cold; for according to the theory, the surface of the cold body which radiates least caloric at a given temperature, that is, the metallic surface, ought to produce the greatest cold, while the fact is precisely the reverse. Pictet advanced a different hypothesis founded on the assumption, that while an equality of temperature exists among a number of contiguous bodies, the caloric is quiescent, or, rather, is in an equality of tension among them all, and there is no radiation from any of them; but when one, at a low temperature is introduced, caloric radiates towards it to restore the equilibrium. Hence the placing the cold body in the focus of the mirror, causes radiation from the bulb of the thermometer in the opposite focus, the mirrors serving to reflect it, and concentrate the effect, an explanation not liable to the difficulty which attends the other, for the radiation from the thermometer taking place in consequence of the action of the cold surface, will be regulated by it, and that surface which absorbs radiant caloric most readily, that is the blackened surface, will, in consequence of this, produce the greatest frigorific effect. Mr Leslie has applied his theory of aerial pulsations to the same phenomenon,—the cold surface being supposed to abstract caloric from the contiguous layer of air, whence a momentary contraction follows; and a chain of pulsations, accompanied with discharges of heat, is established to the cold body by the medium of the mirrors from the thermometer. This hypothesis will of course be adopted only if the general theory of radiant heat depending on aerial pulsations were received.

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SECT. IV.—*On the Comparative Quantities of Caloric contained in Bodies.*

CALORIC has a tendency to diffuse itself over matter until it produce an equilibrium of temperature. Hence, when a number of bodies unequally heated are placed near each other, a communication of it takes place, until a common temperature is established among them.

From this tendency to form an equality of temperature, it might perhaps be inferred, that caloric diffuses itself equally over matter; that it will therefore be contained in bodies in quantity proportional to the quantity of matter, or that equal weights of different portions of matter will contain at the same temperature equal quantities of this power.

This law is observed in the distribution of caloric in homogeneous bodies; different portions of the same kind of matter containing it proportional to their temperatures and quantities of matter; or at least the deviation, with regard to temperature, is inconsiderable, if it even exist.

But in heterogeneous bodies a different law is observed; each contains a quantity peculiar to itself, requisite to produce its temperature; nor are there perhaps any two bodies, which, in equal weights and at equal temperatures, contain the same quantity of caloric. This was first observed by Boerhaave, with regard to quicksilver and water. The subject was prosecuted by Black, Wilcke, Irvine, and Crawford; and from their researches the general law has been established, that at any temperature, different bodies,

in equal quantities, whether estimated by weight or volume, contain unequal quantities of caloric.

This truth is established, when we attend to the augmentation of temperature in different bodies exposed to a common source of heat. They are, after a certain time, raised to a common temperature; but in suffering this rise, it will be found that they have absorbed very different quantities of caloric. Supposing, therefore, that at the commencement of the experiment they contained the same quantity, they must, at the temperature to which they are elevated, contain unequal quantities. But it might equally be proved, that their quantities must have been unequal at the temperature from which they were raised; for in beginning the experiment lower in the scale of heat, they would have required unequal quantities to raise them to this; and this arising from some property in the bodies themselves, which will always continue to operate, we may conclude that at any temperature the quantities they contain are unequal. The same conclusion is established by communicating an equal quantity of caloric to equal quantities of two bodies at the same temperature,—water and quicksilver for example; the augmentation of temperature which this will produce will be very different in each; it will amount to 28 degrees in the quicksilver, when it is only one in the water: we infer, therefore, that water requires 28 times more caloric than quicksilver to raise its temperature, and, of course, that at a given temperature it contains a quantity so much larger.

The general form of experiment by which this truth is demonstrated, and by which also the comparative quantities of caloric that bodies contain are determined, consists in mixing together determinate quantities of bodies at dif-

ferent temperatures, and observing the result; for the hotter communicating a portion of its caloric to the colder, we can, from the temperature that is established in the mixture, discover how much the temperature of the one has been diminished by the abstraction of this caloric, and how much that of the other has been raised by its communication, and, of course, we discover what quantity each requires to produce a certain change.

In homogeneous bodies, the temperature produced by the mixture of equal portions of them at different temperatures is the arithmetical mean between the temperature of each; the excess of caloric which the one contains above the other being equally divided between them, and producing the same rise of temperature in the one portion, as it does of reduction of temperature in the other. But when the same experiment is made with two heterogeneous bodies, the result is different; the temperature produced never being the mean of the two original temperatures. Thus, if one pound of water, at the temperature of 156, be mixed with one pound of mercury at the temperature of 40, the temperature which results is not the arithmetical mean, 98, but is not less than 152. This proves, that the change of temperature produced in the one by a certain quantity of caloric is entirely different from that produced in the other by the same quantity; for the water in this experiment having had its temperature reduced from 156 to 152, has suffered a reduction of only 4 degrees; but the caloric which produced these having been communicated to the mercury has raised its temperature not less than 112 degrees. The quantity of caloric, therefore, necessary to raise the temperature of one pound of water 4 degrees, is sufficient to raise that of an equal weight of mercury

112 degrees; or the quantity requisite to raise the temperature of one of these fluids one degree, raises the other 28. This will be the case at every temperature; and therefore at any point in the scale of heat, the quantity of caloric contained in water is to that contained in the same weight of mercury as 28 to 1.

If the experiment is varied by mixing water at a low, and mercury at a high temperature, the result is the same. If one pound of mercury, at 156, be mixed with one pound of water at 40, the temperature produced is 44. The mercury has lost a quantity of caloric, which has reduced its temperature 112 degrees, and this quantity has raised that of the water 4. In this manner, when equal weights of two different bodies are mixed together, the temperature produced is always nearer to the temperature of that body which contains the greatest quantity of caloric, because it requires the greatest quantity to produce in its temperature any change. The proportion is also indicated by the experiment; the comparative quantities of caloric contained in the two bodies being in the inverse ratio to the change of temperature in each by their mixture. The general formula, therefore, is to multiply the weight of each body by the number of degrees between its original temperature, and the common temperature obtained by their mixture. The comparative quantities of caloric they contain are inversely as the products.

When, instead of comparing the quantities of caloric which equal *weights* of different bodies contain, we compare the quantities contained in equal *volumes*, we find that a similar difference exists. Thus the quantity of caloric necessary to raise the temperature of a given volume of water any number of degrees, is to that necessary to raise an

equal volume of mercury the same number of degrees, as 28 to 1. This is therefore the proportion between the comparative quantities of caloric which these two bodies contain, estimated by their volumes; and similar differences exist with respect to every other kind of matter. The comparative quantities of caloric in bodies are usually estimated from equal weights; the experiments for this purpose being more easily executed with accuracy, than those by which they are estimated from equal volumes.

In making these experiments on solid bodies, the solid, heated to a certain temperature, generally to  $212^{\circ}$ , by immersion in boiling water, is transferred into a measured portion of cold water, and the change of temperature in each is observed. In experiments in which water would enter into chemical combination with the body submitted to trial, some other substance must be used. In this mode a very extensive series of experiments was executed with great care by Dr Crawford; others were performed by Irvine and Wilcke.

It is however difficult of execution so as to attain perfect accuracy, from several sources of error to which it is exposed. A certain time is required before the common temperature is established, during which, part of the heat is abstracted by the vessel, and by the external air; and this is different in different cases, being influenced by the difference of specific gravity in the substances operated on, the facility with which they mix, their conducting powers, the quantities operated on, and the agitation communicated. Hence other methods have been proposed.

The principal of these is by an instrument contrived by Lavoisier and Laplace. Ice, in melting, absorbs a quantity of caloric, which does not raise its temperature; this

quantity being uniformly the same, or equal to what would raise the temperature of the same weight of ice-cold water 135 degrees of Fahrenheit's scale. If, therefore, any body at a high temperature be inclosed in a sphere of ice, so that the caloric it gives out in cooling is communicated entirely to the ice, the quantity which has been given out may be inferred from the quantity of ice melted, or water produced. On this is founded the construction of the Calorimeter, represented Plate II. Fig. 10. It consists of three vessels, A, B, C, adapted to each other, and inserted the one within the other, so as to leave a cavity between the sides of each. A is a cage of iron net-work, designed to contain the body subjected to experiment, which, if solid, is placed within it, heated to a certain temperature; if liquid, is inclosed in a glass matrass; the second vessel, B, is designed to contain the ice, broken into small pieces, and supported on an iron-grating at the bottom, through which the water filtrates, and is conveyed off by a pipe with a stop-cock *a*, which comes from the bottom of the vessel: it has a double cover *b*, also adapted to it, capable of containing ice, the under part of which is perforated, so that the water formed from the melting of the ice it contains may drop into the cavity, and be collected to be measured. The third vessel, C, is similar in its construction to the second; it is filled with pounded ice, and the intention of it is to prevent the agency of the external atmosphere, which, if above 32°, would communicate caloric to the ice, contribute to its fusion, and prevent the quantity of water produced from being an accurate measure of the quantity of caloric which the hot body had given out; or if below 32°, would abstract caloric, and lessen the quantity that would be melted.



This method is free from those sources of error to which the mode by mixture is liable. But it is exposed to others, which render its accuracy doubtful. It is difficult to estimate the quantity of water produced from the fusion of the ice; for a portion of it is retained by capillary attraction in the interstices of the mass, and from some experiments it appears, that a portion of the water produced in the upper part of the apparatus, in filtrating through the ice beneath, is again congealed, probably from the influence of the force of cohesion exerted from the surfaces of the fragments of ice.

The comparative quantities of caloric in bodies have been attempted to be estimated from observing the times equal volumes of them require to cool through a certain interval of the thermometric scale, the times being as the quantities estimated by the volume, and, if divided by the specific gravity of the substance operated on, as estimated by the weight. But the principle of this method appears not quite correct, the times of cooling being influenced by other circumstances, and particularly by the conducting and radiating power.

Some methods have been employed peculiar to the aerial fluids. The difficulties in ascertaining the quantities of caloric, corresponding with the changes of temperature in these by mixture, are extremely great, from the smallness of the quantity we can operate on, compared with the volume the air occupies: and in Dr. Crawford's experiments, by this method, it required instruments extremely delicate, and very minute precautions to guard against errors. In the mode by the calorimeter, the errors from this source are somewhat diminished, from the quantity operated on being larger; the aerial fluid being passed through the in-

strument by a spiral tube, the temperature as it enters and passes out being ascertained by thermometers. Mr Leslie observed, that when a portion of air is rarified in a vessel, and time is allowed for its recovering the temperature of the surrounding medium, on admitting suddenly another portion of air into the partial vacuum, the rarified air is compressed; it hence gives out a quantity of caloric, and this, communicated to the air which has been admitted, raises its temperature. But the rise will be less, as this air requires more caloric to produce in it a given change of temperature; and therefore in operating on different aërial fluids, the comparative quantities may be discovered from the respective elevations of temperature. The method is extremely ingenious, but attended with considerable difficulties in the execution, so as to attain accuracy, and accordingly the results have been stated differently, from a repetition of the experiments by Gay-Lussac.

The comparative quantities of caloric in the aërial fluids have lately been made the subject of experiment by Messrs Delaroche and Berard. Their method consists essentially in causing a current of the air submitted to trial to pass, at a certain high temperature, through a spiral tube placed in a cylinder of copper filled with water, ascertaining the temperature of the air as it enters the spiral tube, and as it issues from it, and finding how much the temperature of the water is raised by the reduction of the temperature of the air. The results they have given are very different from those of Crawford. Their method has the advantage, that a larger quantity of air is operated on; but it is more complicated; and is liable to sources of fallacy, in applying a uniform current of air without variations of pressure, determining its temperature before and after it

enters the tube, and excluding the influence of the surrounding medium. Their results are not therefore to be implicitly received in opposition to those of Crawford, whose experiments were conducted with great care and precision, especially as some of these results are at variance with some general principles which rest on a very strict and extensive induction.

The property by which different bodies contain their respective quantities of caloric, has been termed the Capacity for Heat, or, adapting the expression to the modern nomenclature, the Capacity of a body for Caloric. This term is not designed to imply any theory with regard to the cause of this property, or the nature of it; nor does it present, as has been alledged, a vague or obscure idea. It is simply a general expression, to denote the property, in consequence of which, bodies contain at any given temperature, in equal quantities, peculiar quantities of caloric. That they do so is unquestionable, and it is convenient to have a general term by which this can be expressed. The quantity contained in a body, and peculiar to it, has been named the Comparative, or the Specific heat. The phrase Specific Caloric is generally adopted.

What the nature of this property is, or from what cause different bodies require different quantities of caloric, to produce in them temperature to the same extent, is not easily determined. It is in general true, that bodies which are rare, have capacities for caloric greater than those which are more dense. It is even found, that we augment the capacity by diminishing the density of any body; the rarefaction of an aerial fluid, for example, in which this can be done to the greatest extent, being attended with a reduction of temperature from enlargement of capacity,

and its condensation being followed by the opposite result. In liquids or in solids, condensation is likewise accompanied with a similar change from the same cause. But, although there is this general connection between the rarity of a body, and its capacity for caloric, it is not invariable or proportional; if it were, indeed, the quantities of caloric contained in bodies at given temperatures would be as their volumes,—a law which is far from being observed.

There must, therefore, be some other cause by which this is modified. If we regard caloric as a material substance subject to attraction, the attraction exerted to it by the substance in which it is contained might be supposed to be the cause modifying the law, which would otherwise be observed in its distribution, and by which, in consequence of its perfect elasticity, it would be contained in bodies, in quantities proportional to the void spaces between their particles. But the relations of this agent are so imperfectly known, that no theory in which we can place much confidence can be given, and the fact must merely be stated as an ultimate one, that bodies require specific quantities of caloric for the production of temperature.

A question of some interest is, whether the relation of each body to caloric is the same at all temperatures; in other words, are their capacities uniform and permanent. It is possible this may not be the case; but that the rise of temperature itself, and the effects by which it is accompanied may give rise to a change in the relation, so that a greater or less quantity of caloric may be required to produce a given rise of temperature, at a high than at a low part of the scale of heat. When the mechanical condition of a body is changed, when it passes to the fluid or aëri-

form state, this change of capacity actually happens. Does a similar change, though less perceptible at any particular stage, happen from the progressive expansion to which elevation of temperature gives rise?

The experiment by which this has been attempted to be determined, consists in mixing equal portions of the same body at different temperatures: if the capacity is permanent, the resulting temperature ought to be the arithmetical mean; for the hotter portion communicating the half of its excess of caloric to the colder, the one, if the capacity is the same in each, ought to suffer just as great a reduction as the other sustains an elevation of temperature. But if the one portion have a greater capacity than the other, then the change it suffers must be less considerable, and the resulting temperature must approach nearer to its temperature than to that of the other, and of course deviate from the mean. The experiment is difficult of execution, so as to attain perfect accuracy, especially as no great range of temperature can be submitted to experiment, and as the difference in capacity, therefore, if it exist, cannot be expected to be great. Dr Crawford from his experiments was disposed to conclude, that the capacities of bodies are permanent; but he perhaps was somewhat influenced in drawing this conclusion by theoretical views. It appears to be more probable from theory, that the capacity should be progressive with regard to temperature, or should be greater in the higher than in the lower portions of the scale of heat; for this property is unquestionably to a certain extent connected with the density of bodies, being under a general point of view greater as they are less dense, and being increased in any body when its volume is enlarged; and, as rise of temperature is accompanied with enlarge-

ment of volume, this may be expected to give rise to augmentation of capacity. In any interval of temperature which we can measure this may not be considerable; but considered in relation to the whole scale, we cannot conjecture its amount, for we know not the extent of expansion from the commencement of the scale.

There is even reason to doubt if the permanence of capacity be established within the range of temperature at which bodies can be easily submitted to experiment. The conclusion of Crawford rested very much on the previous assumption of the accuracy of the thermometer, and is invalidated if the expansions of the thermometrical liquid are progressive with regard to temperature, as this would counterbalance the effect from enlargement of capacity, if this happened, and give rise to an adjustment whence the effect of neither might be apparent. And, with regard to some bodies, it is ascertained, even by Crawford's own experiments, as well as by those of Gadolin, that the capacities are not permanent, but increase with the temperature, rendering therefore more probable the conclusion that this is a general result.

The law now illustrated with regard to the distribution of caloric in bodies is of the first importance, as giving the theory of changes of temperature from chemical action. Combination is almost invariably attended with a change of capacity, the capacity of the compound not being the mean of the capacities of the bodies combined. When it is greater the temperature falls; when it is less the temperature is raised. On this principle are explained the production of heat in combustion, in respiration, and in a number of chemical combinations, and the production of cold in the solutions of salts in water, and in what are denominated

freezing mixtures. The objections which have been made to this theory have in general arisen from misconception of it. Some late observations, however, render it not improbable that the evolution of heat may, as is to be afterwards stated, be connected with changes of electric excitation; but still changes of capacity have an important effect in its production, and in many cases have been experimentally ascertained.

From the nature of the methods by which the quantities of caloric which bodies contain are ascertained, it is evident that we discover the comparative, not the absolute quantities. We find only how much caloric a body gives out, or absorbs, during a certain change of temperature; and by observing the change of temperature which the body from which it has received, or to which it has given caloric, suffers, we may ascertain the comparative quantities necessary to produce equal changes of temperature in these bodies. But we do not learn the proportion which the quantity in each bears to the whole caloric which it contains. Hence it becomes necessary to fix on one body as a standard to which the others may be referred. Water has been chosen as this standard; its capacity is stated at the term of 1000, and with this the capacities of other bodies are compared. Thus the capacity of arterial blood is 1030, indicating, that if at any temperature a certain quantity of water contain 1000 degrees of caloric, the same quantity of arterial blood at the same temperature will contain 1030 degrees. The capacities are usually referred to equal weights, not to equal volumes of bodies; but the latter are easily found, by multiplying the number expressing the specific caloric of any body estimated by its weight, by the number which denotes the specific gravity of the body; the product is the specific caloric estimated by the volume.

In the Appendix will be found a table, in which the capacities of a number of bodies are stated as established on several authorities.

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SECT. V.—*Of the Quantities of Caloric which Different Forms of the same Body contain.*

BESIDES the general law illustrated in the preceding section, that different bodies, at equal temperatures, contain unequal quantities of caloric, it has further been established, that a similar law exists with respect to the same body in its different states of aggregation: a body in the fluid form contains more caloric, or requires a larger quantity to produce a given change of temperature in it, than it does while solid; and in the state of air or vapour, it requires still more caloric than it does in the liquid form. Hence, when a solid is melted, or a liquid is converted into vapour, a quantity of caloric is absorbed, which has no effect in producing augmentation of temperature. This gives rise to the phenomena of what has been denominated Latent Heat, for the discovery of which we are indebted to Dr Black.

The truth of the fact with regard to this absorption of caloric, is sufficiently evident, when the phenomena attending liquefaction and vaporization are attentively examined. When caloric is communicated to a solid body, increase of temperature is produced, and this continues to proceed while the caloric continues to be added, until the body arrives at its melting point: but whenever it begins to melt, the rise of temperature ceases, though the addition of caloric be continued as before; and the fluid, as it forms, re-



mains at one point until the fusion is completed. In this case, then, it is evident, that a quantity of caloric disappears; for it continues to be added to the body, but has no effect in raising its temperature. The case is the same when a liquid is converted into vapour. Its temperature is progressively raised to the point at which it begins to boil, by the communication of caloric; but though the communication be still continued, the temperature, neither of the fluid which is evaporating, nor of the vapour rising from it, is farther raised, but remains stationary at that degree in the thermometrical scale at which the conversion into vapour commenced, until the whole be evaporated. It is evident, therefore, that in this case also a quantity of caloric is absorbed by the vapour formed, which has no effect in raising its temperature. The liquid or vapour, after it is formed, has its temperature raised by additions of caloric. It was from considering these facts, that Dr Black concluded, that during liquefaction and vaporization a quantity of caloric is lost, becomes latent or passes into the body without raising its temperature,—a conclusion which he established by very simple but decisive experiments, affording an admirable example of chemical research.

To prove it with regard to liquefaction, he placed equal portions of water in two vessels, cooling the one portion to  $32^{\circ}$  without freezing, and causing the other to freeze, but taking care that the ice should not be lower than this temperature. They were equally exposed to an atmosphere somewhat warmer, from which of course they received heat,—the temperature of the water soon rose, and, at the end of half an hour, the rise amounted to  $7^{\circ}$ . But the temperature of the ice remained stationary at  $32$ , though it must have received caloric equally with the other. It

+ It does not appear, however, that the temperature of the ice rises after the commencement of fusion, or vaporization.



little salt to a portion of water, so as to enable it to sustain reduction of temperature below  $32^{\circ}$  without freezing, he exposed it; with a similar portion of water in another vessel, to a cold atmosphere. Both were cooled with regularity to  $32^{\circ}$ ; but at this temperature the pure water remained stationary, while that with the salt dissolved in it continued to fall lower; the former must equally have suffered an abstraction of caloric with the latter, but caloric being evolved from its congelation prevented its fall. In another experiment, Dr Black cooled water, by avoiding agitation; a number of degrees below its usual freezing point  $32^{\circ}$ : on agitating it, it congealed, and the temperature instantly rose to  $32^{\circ}$  from the evolution of the caloric peculiar to it in the state of water.

Similar experiments were made by Dr Irvine on spermaceti, wax, and tin; and they have since been extended to other bodies; and with regard to all the same fact has been established,—a portion of caloric peculiar to each being absorbed when the body melts, without causing any rise of temperature, and this portion of caloric concealed in the liquid becoming sensible when it is congealed.

Dr Black demonstrated, that a similar phenomenon accompanies the other change of state to which bodies are subject, that into vapour or air, a quantity of caloric being absorbed by the body passing into this state without raising its temperature, and being evolved when it returns to the liquid form. This is evident from the usual phenomena of vaporization attentively examined, neither the liquid nor the vapour rising from it suffering any increase of temperature after the ebullition has commenced, though caloric be constantly communicated. It was farther esta-

*imagined since the other experiment does not appear satisfactory for the same reason. Since the latent caloric is now known to be absorbed in order to produce a permanent increase of temperature, as in the case of the latent heat of fusion, it is not surprising that the latent heat of fusion is not the same as the latent heat of vaporization.*

lished by experiments ascertaining it with more accuracy, or placing it in a clearer light.

A portion of water in a cylindrical tin vessel placed on a heated iron plate, was raised in temperature from  $50^{\circ}$  to  $212^{\circ}$  in four minutes, when it began to boil; in that time, therefore, it had received a quantity of caloric capable of raising its temperature  $162^{\circ}$ . It continued to boil, and twenty minutes elapsed before it was dissipated; neither its temperature, nor that of the vapour into which it was converted, rose above  $212^{\circ}$ , yet it must have continued to receive caloric as before; that is, at the rate of  $162^{\circ}$  every four minutes; of course, in its vaporization, a quantity of caloric had been absorbed, which, applied at once, would have been equal to raising its temperature  $810^{\circ}$ .

A liquid heated under pressure may have its temperature raised above its usual boiling point, the transition into vapour being prevented by the pressure. A quantity of water included in a strong phial closely corked, with a thermometer included, was heated to  $232^{\circ}$ : the cork was suddenly withdrawn, a small quantity only of vapour rushed out, and the remaining water instantly fell to  $212^{\circ}$ . This experiment Mr Watt repeated on a much larger scale, water being heated in a copper digester with a safety valve to a much higher temperature; yet, on opening the valve, instead of the whole escaping in vapour, not more than one-third of it assumed this state, and the temperature of the remaining portion sunk as in the preceding experiment.

A similar absorption of caloric attends the vaporization of volatile liquids at a common temperature, producing therefore sensible cold, greater as the liquid is more volatile, or as the change is accelerated, as Cullen observed.

The caloric which is thus absorbed in the transition of a body to the state of vapour, is again evolved when the vapour is condensed. Dr Black found, that when steam, at the temperature of  $212^{\circ}$ , is condensed by being received in cold water, the temperature of this is much more raised, than by the communication of a weight of water at  $212^{\circ}$  equal to that of the steam. And Mr Watt having condensed steam in a metallic tube, by suddenly forcing down a piston adapted to it, the end of the tube being placed in water, found a quantity of caloric to be communicated to the water, equal to what would have raised the temperature of a portion of it equal in weight to the steam  $848$  degrees. Yet the temperature of the tube and the included steam, previous to the condensation, was only  $212^{\circ}$ .

All these facts prove the truth of the general proposition, that when bodies pass from the solid to the fluid, or from the fluid to the gaseous state, a quantity of caloric is absorbed, which has no effect in raising the temperature of the body in its new form, this caloric being again evolved when the body returns to its former state. This portion of caloric absorbed during these changes, and not discoverable by the usual effect of raising temperature, Dr Black named Latent Heat, in opposition to the portion by which temperature is produced, and which he denominated Sensible Heat.

In assigning the cause of these phenomena, Dr Black supposed, that the caloric which disappears or becomes latent, produces the change of form, losing at the same time its own characteristic properties, probably by entering into a species of combination with the matter on which it operates. "Fluidity," says he, "I consider as depending immediately and inseparably on a certain quantity of

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\* What weight of steam would give a weight of water  $100$  lbs, on the whole, being  $100$  lbs? — Mr Watt & the late Dr Black found a quantity of caloric in the transition of water to steam.

the matter of heat which is combined with the fluid body in a particular manner, so as not to be communicable to a thermometer or to other bodies, but capable of being extricated again by other methods, and of re-assuming the form of moveable or communicable heat." And, again, with regard to vaporization, "when a fluid body is raised to its boiling temperature by the continual and copious application of heat, its particles suddenly attract to themselves a great quantity of heat, and by this combination their mutual relation is so changed, that they no longer attract each other, but separating, compose a fluid elastic and expansive like air. This new form of aggregation, (taking the example of water,) is the effect of a new combination of heat with the primary particles of water, and is a sufficient indication of this union, in the same manner as fluidity was a sufficient mark of a sudden and copious combination of heat with the particles of ice."

A very different theory of these phenomena, and more approaching to a philosophical generalization, was advanced by Dr Irvine. Temperature depends not merely on the action of caloric, but on its action modified by that peculiar relation of bodies to it which we denominate their capacity. If the capacity of a body be enlarged, the quantity of caloric communicated to it remaining the same, its temperature must fall; if the capacity be diminished under the same condition, its temperature must rise; or if the capacity be enlarged while caloric is proportionally communicated, this caloric will be absorbed by the body, and remain in it without any increase of temperature. Now this last result Dr Irvine conceived to happen in fluidity and vaporization. The sensible caloric communicated, and raising the temperature of the body to its melt-

ing, or to its vaporific point, weakens progressively its cohesion, and at length so far changes its state of aggregation, as to cause a new arrangement of its parts, constituting first fluidity, and afterwards the state of vapour or air. These changes Dr Irvine supposed to be accompanied with a change of capacity, the capacity of the body in its liquid being greater than in its solid state, and becoming still larger in the state of vapour. If this be admitted, it necessarily follows, that a quantity of caloric must be absorbed by the body in passing into the liquid and aerial forms, which will have no effect in augmenting its temperature; and which, of course, is not discoverable in it by the thermometer. But there is no reason to believe that this caloric has lost its properties, has entered into any peculiar combination with the body, or is in any state different from the rest of the caloric it contains. It goes with that caloric to sustain the temperature, and it has been absorbed without raising temperature, merely because the capacity of the body has been enlarged; and when the capacity is diminished, as happens in the reverse change of form, it is, of course, again evolved. A body in one form, in a word, contains more caloric than in another form at a given temperature, exactly as one body contains more than another does; or, according to this theory, the cause why water contains more caloric than ice at  $32^{\circ}$ , is the same as that by which water contains more caloric than quicksilver; and were it possible to convert quicksilver into water by a process similar to that by which we convert ice into water, we should have precisely the phenomena of latent heat.

The whole question, therefore, on this subject, is with regard to the assumption on which the theory rests, whe-

ther an augmentation of capacity accompanies liquefaction and vaporization or not. No doubt can remain of its superiority *a priori* to the opinion of Black. It explains the phenomena; for it is obvious, that if by fusion or vaporization the capacity of a body be enlarged, either its temperature must fall, or caloric must be absorbed without producing any rise of temperature: the first cannot happen; for, in this case, the temperature of the body falling below its fusing or vaporific point, the change of form could not proceed: the second event, therefore, must be that which will occur, or if, by applying caloric, we raise and preserve the temperature sufficiently high to cause the transition of form to proceed, if this be accompanied with an increase of capacity, the caloric applied must be absorbed and become latent, or occasion no increase of temperature. And the theory has farther the very important advantage, that while the opposite system is an insulated hypothesis, framed to account for this particular case, Irvine's is an extension by generalization of a law, proved to exist with regard to different bodies, and not unlikely to operate in a similar manner on the same body in different forms.

The determination of the fact occupied the attention of Dr Irvine for a series of years, the experiments by which only it could be decided being attended with peculiar difficulties; for, in determining the capacity of the body, either in the solid or liquid state, it is necessary, that in the progress of the experiment it should not change its form. Ice, therefore, must be operated on at temperatures below 32°, and water at temperatures above this. Dr Irvine employed the medium of a third substance, such as quicksilver, river-sand, or iron-filings, which he added to



each, and determined the capacity in the usual manner; and he uniformly found, that the capacity of water is greater than that of ice, and in a ratio which he inferred, from the average of his experiments, to be as 10 to 8. A similar augmentation of capacity Dr Crawford found to take place when water is converted into vapour. It is proved then, that the change in the relation of the body to caloric is not confined, as Dr Black's hypothesis supposes, to the moment of liquefaction or vaporisation, but at these changes the relation is so altered, that henceforth the liquid requires more caloric than the solid did to raise it every degree of the thermometric scale, and the vapour, in like manner, requires more than the liquid. In consequence of this, an absorption of caloric must take place at the moment of change, sufficient with the caloric the body contained, to keep up the existing temperature from the point of absolute privation, according to the enlarged capacity of the body in its new state. And with the admission of these facts, the one theory is demonstrated, while the other cannot be maintained.

The only difficulty that has been urged against the theory of Irvine, of any seeming importance, is that of accounting for the change of form; for since the temperature of the liquid is not sensibly greater than that of the solid from which it is formed, nor that of the vapour greater than that of the liquid from which it rises, it has been contended, that the change cannot be ascribed to the operation of sensible caloric, and must therefore be ascribed to the action of at least a portion of that which becomes latent. The difficulty, however, is in a great measure, perhaps entirely, obviated, by considering the change of form as arising from the expansive operation of caloric, increasing as it is accumulated, until it sufficiently modify or subvert the force

of cohesion to admit of fluidity and vaporization being established; and this being progressively exerted, the ultimate effect may take place at a point in the scale of temperature indivisible, so that we shall be unable to discover a difference of temperature on the one hand or on the other.

This view of the cause of the change of form is confirmed, by finding that the change is produced by causes which must operate solely by altering the distances at which the particles of bodies are placed. Thus, the transition into vapour is effected by withdrawing pressure, which can be an antagonist only to the expansive operation of sensible caloric: Or, by applying pressure, a vapour may be reduced to the liquid state, though this pressure can have only a mechanical effect, approximating the particles, and cannot subvert any chemical combination of caloric, did it exist.

It may therefore be concluded, that the absorption of caloric which accompanies liquefaction and vaporisation, is owing not to any chemical combination, but to the enlarged capacity which the body acquires by a change of form. It may be supposed, indeed, that the difficulty in this view of the subject is only avoided, not removed. May not this difference of capacity in bodies, in whatever state they exist, proceed from a chemical combination of caloric? By saying that different bodies, or different forms of the same body, have different capacities for caloric, the fact is merely expressed, that in equal quantities, and at equal temperatures, they contain unequal quantities of this power. But the cause of this is not assigned. May it not be chemical combination of part of the caloric, of that part of it in each body which amounts to the difference of the quantity it contains, compared with another? This opinion is refuted by the consideration, that, were it true, the quan-

tity of free caloric, or caloric of temperature, ought in all bodies to be the same, and that consequently in equal changes of temperature, equal quantities of caloric ought to be absorbed, or given out by all, since the very principle which is assumed is, that the cause of the difference in the absolute quantities of caloric which bodies contain is, that that portion in one body, which exceeds what is contained in another, exists in it in a state of chemical combination.

Whether, therefore, the question be considered as relating to the cause, why different bodies contain, at the same temperature, unequal quantities of caloric, or to the cause why different bodies of the same body follow the same law, in neither case is it probable that a chemical combination of part of that caloric gives rise to the difference. *And as the phenomena are in both cases the same, they must be ascribed to the same cause.* Until this is discovered, the general fact ought merely to be expressed: Caloric, whatever may be its nature, is to be considered as a power diffused over matter, as the cause of that state of bodies termed their temperature, as having a tendency to diffuse itself, until a common temperature is formed; but for the production of this temperature in different bodies, and in different forms of the same body, unequal quantities of this power are required. If it be a material agent, the difference in the quantity contained may be owing to the specific attraction exerted by each body; but still this attraction is merely the force by which the whole quantity is retained, and does not operate more on one portion than on another.

Some philosophers of eminence, indeed, without alleging that the difference in the quantities of caloric in different bodies, or the absorption of it during liquefaction

and vaporization, is owing to chemical combinations, have supposed, that there may be a portion of caloric existing in bodies in such a state of combination. Lavoisier and La Place inclined to this opinion, from finding by experiment, that in different cases of chemical union, or of change of form, the quantity of caloric rendered sensible does not correspond with the changes of capacity that take place, but is sometimes greater, at other times less; whence they concluded, that a portion of caloric must exist in bodies in some other state, and probably in more intimate combination. They admit, however, that trivial errors in the estimation of the capacities might have given rise to the apparently discordant results they obtained; and when the sources of fallacy attending such experiments are considered, it will appear not improbable that such errors must have been present. Irvine and Crawford devoted much attention to this investigation, and uniformly found, that when bodies produce heat by mutual action, or change of form, their capacities are diminished, and that, on the contrary, when they produce cold their capacities are increased; nor were the results inconsistent with the law of the changes of temperature being proportional to the increase or diminution of capacity, making allowance for the inaccuracies to which such experiments are unavoidably liable. Gadolin executed a very extensive series of experiments with the same view, and drew from them the same conclusion. Nor are there any facts which, when duly considered, can be regarded as affording proof, that any portion of caloric exists in bodies chemically combined: though arguments in support of it are not unfrequently stated, arising from misconception of the subject. It is therefore necessary to remark, that the hypothesis of

combined caloric rests on no just grounds. The different quantities of caloric contained in bodies, regulated by what we name their capacities, cannot be referred to the operation of any peculiar force different from that by which the whole quantity of caloric is contained; neither can the absorption and latent state of the caloric, absorbed in liquefaction and vaporization, be referred to this cause. And we have no reason to believe that any other portion of caloric exists in bodies in a combined state. The agency and relations of this power are indeed so peculiar, that, even admitting its materiality, we can place little reliance on any conclusion with regard to its mode of existence, not established by direct evidence, but resting on analogies transferred from ponderable substances; and in the present state of the science, the hypothesis of combined caloric can only be suggested from very limited views.

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FROM the enlargement of capacity and consequent absorption of caloric, which attends liquefaction and vaporization, some interesting applications both to natural phenomena and to purposes of utility are derived.

Thus it explains the fixity and uniformity of the temperature at which bodies melt. Ice melts at  $32^{\circ}$  of Fahrenheit, and, when raised to this temperature, the farther communication of caloric, however rapid, has no effect in raising its temperature, till the whole is converted into water; since, as quickly as the ice is melted, as quickly is the

caloric absorbed by the fluid. Were it not for this absorption of caloric, the liquefaction of ice and snow, in colder climates, at the approach of spring, would take place almost instantaneously, when the temperature of the atmosphere rose above  $32^{\circ}$ ; whereas, from this, the melting is gradual and progressive; the water that is formed is distributed more slowly, and the too sudden rise of temperature, which in such climates would prove fatal to vegetables, is prevented. The reverse of this, too, or the extrication of caloric, when water is converted into ice, is equally beneficial; since, were it otherwise, the freezing of large collections of water would be extremely rapid when the temperature of the atmosphere fell below  $32^{\circ}$ . But, from this extrication, the freezing is gradual, and a large quantity of caloric is given out by the water in passing to the solid state, by which the approaching cold is moderated, and the congelation rendered more slow.

Similar general effects arise from the operation of this law in vaporization. Water evaporates more speedily from the surface of the earth as its temperature is high, but this evaporation is necessarily accompanied with the absorption of caloric. Hence it operates with equal effect in moderating excessive heat. Again, when the vapour of the atmosphere is condensed by cold, in passing into the liquid state, it gives out the caloric it had received, and is equally beneficial in moderating the excess of cold.

Artificial refrigeration depends on the same principle. When water filtrates slowly through porous earthen vessels, so as to present an extensive humid surface to the atmosphere, it passes rapidly into vapour, and in this vaporization absorbs so much caloric as to produce a considerable degree of cold. Liquors are cooled, and in warm

climates ice is formed, by arrangements of this kind, even when the temperature of the atmosphere is above  $32^{\circ}$ .

The theory of freezing mixtures is likewise derived from the doctrine of latent caloric. These mixtures consist of saline substances, which, at the common temperature, by their mutual chemical action, pass rapidly into the fluid form, or are capable of being rapidly dissolved in water, and the transition of this large quantity of solid matter to fluidity causes an absorption of caloric, producing cold more or less intense.

The use of steam as a vehicle and source of heat affords an example of the scientific application of these principles. By conveying it into water, it is condensed, and by the evolution of the latent caloric, which follows from this, the temperature of the water is raised, so as soon to arrive at  $212^{\circ}$ . Where large quantities of water are to be heated, this method has superior advantages, as by having a common boiler, from which the vapour is conveyed by tubes, the loss of heat is less than if fire was applied to different vessels, and the vessels are subject to less wear, and may be constructed at less expence. Another application of the same principles is that of heating apartments by conveying steam through tubes. The steam in its progress is condensed gradually, and gives out its latent caloric, so as to produce an equable warmth.

The modern improvements in the Steam-engine, as they originated from Dr Black's discovery, so they afford a very striking exemplification of the doctrine of latent caloric. In the engine wrought previous to the improvements of Mr Watt, the steam was received into a cylinder, to which a piston was adapted, which was raised by the introduction of steam: this was condensed by a jet of cold water,

and the piston was of course forced down by the pressure of the atmosphere, and by these alternate actions the machine was worked. But this was attended with an immense loss of heat; for by the jet of cold water not only was the steam condensed, but the cylinder was cooled, as it was also by the entrance of the atmospheric air, and the first portion of steam, therefore, that next entered was condensed. At each stroke of the engine this waste is repeated, and thus, according to Mr Watt's calculation, at least half of the steam produced in the boiler is lost. His principal improvements consisted in condensing the steam, not in the cylinder, but in another vessel communicating with it by a pipe with a valve, and in excluding from the cylinder the atmospheric air, and depressing the piston by steam introduced above it, and condensed in the condensing vessel alternately with the steam beneath. The whole can thus be kept at the temperature of  $212^{\circ}$ , and the immense waste of heat in the old method is obviated.

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SECT. VI.—*Of the Absolute Quantity of Caloric in Bodies.*

A PROBLEM which Chemists have sometimes proposed for solution, is that of determining the whole quantity of caloric in bodies, and of course at what distance, measured by thermometrical degrees from a given temperature, the point of absolute privation, or what they have named the real zero, would be placed. It is obvious, that any reduction of temperature that we can command is far distant from the total abstraction of caloric, and it is only by



calculation from certain known facts that the zero can be determined.

The possibility of discovering this occurred to Dr Irvine, and the principles on which his method were founded are extremely simple. Assuming that the caloric contained in bodies is as their capacities, and knowing the difference between the capacity of a body in its different states, for example in its solid and liquid states, it is obvious, that if we ascertain, by experiment, the quantity of caloric which it absorbs or gives out in passing from one state to the other, we can determine the whole quantity of caloric it contains; for the quantity evolved bears a certain proportion to this, which proportion the difference of capacity gives. Thus, if the capacity of water be 10, and that of ice 9, and if the whole quantity of caloric which each contains be as its capacity, then water contains a quantity as 10, ice a quantity as 9, or water contains one-tenth more caloric than ice at the same temperature. This tenth part is given out when water passes into the state of ice; the quantity actually evolved we discover by experiment to be equal to what would raise its temperature  $140^{\circ}$  of Fahrenheit's scale. The water previous to freezing, therefore, contained a quantity equal to ten times this, or a quantity equal to what would elevate its temperature  $1400^{\circ}$ . Of course, at this distance from  $32^{\circ}$  of Fahrenheit, it would be wholly deprived of caloric, or the real zero would be placed; and this would be the same with regard to all bodies measured by thermometrical degrees, according to the capacity of each; for although they contain different quantities, this is only because they require different quantities to produce the same elevation of temperature: the degrees of temperature are the same.

The calculation of Irvine was confirmed by the experiments of Crawford, and also by those of Gadolin, both made on the capacities of bodies combining together, the capacity of the compound formed, and the quantity of caloric absorbed or evolved during the combination. Crawford, by determining the capacity of water, the capacities of its constituent principles, and the quantity of caloric evolved when these combine, found the zero to be at 1532 below the freezing point of water; and Gadolin, from observing the changes of temperature in the solution of muriate of soda in water, and also in the combination of sulphuric acid and water, compared with the capacities of the respective substances, placed it at 1432 below that point. Other chemists, however, have obtained results extremely discordant. In the experiments of Lavoisier and Laplace, the numbers are very remote from those above stated, and from each other; and, in the more recent experiments of Dalton, are so even to a greater extent; the zero being found, from some experiments, at 3000, others at 5000, or at 7000° below the temperature of freezing water. We can place little confidence in any of these calculations; and either the assumption on which the theorem rests, that the quantity of caloric in bodies is as their capacity, is incorrect; or the experiments, so far as relates to the estimation of the capacities, must be liable to sources of error nearly unavoidable, and which, from being multiplied by the calculation, give rise, even though trivial in themselves, to errors so great. The latter is probably the case; for the methods of discovering the capacities of bodies, give us rather approximations than absolutely accurate results.

From the diversity of opinions which have prevailed with

regard to the state in which caloric exists in bodies, several forms of expression have been introduced, and are still in use, which it may be proper to define.

*Free caloric* is caloric in that state in which it expands bodies, and, accumulated to a certain extent, occasions the sensation of heat. It is synonymous with the *sensible heat* of Dr Black, and with the *caloric of temperature* of other chemists.

*Specific caloric* is the quantity of caloric peculiar to any body compared with another, and therefore expresses the relative quantities of caloric contained in equal weights of different bodies at the same temperature. It is synonymous with the *comparative heat* of Dr Crawford. Others have used the phrase *relative heat* in a similar sense. This, however, is employed by Wilcke to denote the specific caloric of a body, estimated, not by the weight, but by the volume.

The disposition or property by which different bodies contain certain quantities of caloric, at any temperature, is termed their *capacity for caloric*.

*Latent caloric, or latent heat*, is the expression used to denote that quantity of caloric which a body absorbs, when it changes its form. *Combined caloric* is that portion supposed to be contained in any body, in a state of chemical combination. The *Absolute heat* of Crawford denotes the whole quantity of caloric which any body contains; and is expressed, according to the modern chemical language, by saying, the absolute quantities of caloric present in bodies.

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**SECT. VII.—Of the Nature of Caloric.**

By the ancient philosophers, heat was considered as a subtle fluid or element; and this opinion was received until the time of Bacon. From observing that the circumstances which cause augmentation of temperature are such as excite motion, and that in general whatever produces motion produces heat, he advanced the hypothesis, that the heated state of bodies depends on vibration of their particles. Though this opinion was adopted by some chemists, particularly by Boyle, Newton, and Macquer, the other, which considers the phenomena of heated bodies as depending on the presence of a peculiar material principle, continued to be more generally received.

The general phenomena which are produced by the action of caloric, are sufficiently explained on the hypothesis of its being a subtle highly elastic fluid, capable of penetrating bodies, with the exception of one familiar phenomenon,—the excitation of heat by friction, percussion, or any species of motion producing vibration in the particles of bodies. On the hypothesis of temperature depending on the presence of a material agent, it is difficult to conceive how it should be raised by the operation of these causes, and it is from this difficulty that the hypothesis of heat depending on motion has originated.

The difficulty has appeared greater, too, since the excitation of temperature by friction has been investigated with more precision; for it appears to be produced without limitation while the friction is applied, and without

any external source whence it may be supplied. Rumford observed, that in the boring of cannon, much heat is rendered sensible by the friction. To ascertain its quantity with more accuracy, he placed a solid cylinder of brass in a trough with water, and applied the borer to it in the usual manner. In an hour the temperature had risen from 60 to 107, and in two hours and a half the water was brought to boil, its quantity being 18 lbs., and the apparatus immersed in it, which was of course likewise heated to 212°, being equal to 15 lbs. This excitation of heat, it was obvious, was not dependent on any action of air, as this was excluded by the manner of making the experiment: the water does not appear to have exerted any chemical agency, as it suffered no change: the caloric, Rumford supposed, could not be derived from the surrounding matter, as this was actually receiving heat from the body submitted to friction, and it could not, he conceives, be derived from this body itself from any diminution of capacity produced by the friction, as the capacity of the borings of the metal he found to be the same with that of the mass of metal. He concluded, therefore, that what was thus furnished, apparently without limitation, could not be material, and that it is difficult to conceive of any thing capable of being excited in the manner the heat was excited and communicated in these experiments, except motion. Experiments giving a similar result were published nearly at the same time by Mr Davy.

If these two hypotheses on the nature of caloric be merely compared together, the superiority evidently belongs to that which regards it as a material principle; for the general phenomena connected with its operation receive a more satisfactory explanation from this assumption, than

from the supposition that heat arises from vibration or motion of the particles of matter. Expansion, fluidity, and vaporization, may be conceived to arise from the introduction of an elastic fluid counteracting the mutual attraction of the particles of matter : this fluid, it is probable *à priori*, may have peculiar relations to different bodies, may therefore be propagated through them with different degrees of facility, be contained in them in a given state in unequal quantities, or may act upon them unequally, so as in equal quantities to produce unequal effects. Considering caloric, on the other hand, as arising from vibration, it is not obvious how this should produce even the most general effect, that of expansion : we do not perceive how, when accumulated to a certain extent, it should give rise to permanent repulsion : we are equally at a loss to account for the law which regulates its distribution in bodies, as producing temperature, or the laws of its communication, which are different from those of motion.

There remains, however, on the doctrine of the materiality of caloric, the difficulty of explaining the excitation of heat by friction. Is the following hypothesis adequate to this? By friction, or similar causes of motion, the particles of bodies are thrown into a state of vibration ; they alternately approach to, and recede from each other. In their approach, the common law with regard to the effect of condensation on temperature must be observed, or heat will be excited ; in the corresponding retrocession, heat will, from the same cause, be absorbed. Is it possible, that in this retrocession, the layer of matter, in the state of vibration, may rather receive caloric from the contiguous layer, and ultimately from the rest of the mass, than re-absorb that which had been evolved in the preceding ap-

proximation, that in this way a current of caloric may flow towards the vibrating surface; and a constant evolution of it be kept up? The possibility of this is established by proving, that an analogous case occurs in which this happens. The excitation of electricity by friction affords it. The surface affording electricity is in a state of vibration from the friction applied to it; and the phenomena of electricity prove, that the electric fluid forced out, probably by the approximation of the particles from the vibration, is not re-absorbed in the following retrocession, but forms an atmosphere around the electric body, or is carried off by the surrounding matter, while a new portion is received from the mass in contact with the excited surface, and ultimately from the earth, so that a constant evolution of it can be continued, while the friction is applied. Caloric may follow the same law, though, from not having that relation which electricity has with regard to conducting and non-conducting matter, this is not so easily established. If such a law operate, it may give rise to similar phenomena, at least to a less extent.

The evolution of caloric, from this cause, is no doubt connected with diminution of capacity; and that this should happen, is even rendered extremely probable, from the effect of condensation on the capacities of bodies, as already illustrated. But this diminution of capacity is only momentary, though constantly renewed; and the experiment, therefore, by Rumford, of ascertaining the capacity after the friction has ceased, is wholly inconclusive. It is farther to be remarked, that a very slight diminution of volume may be sufficient to produce a considerable elevation of temperature. Berthollet has justly remarked, with regard to Rumford's experiment, that a very large

addition of caloric is requisite to produce even a small augmentation of volume in a mass of solid metal, and that of course a small reduction of volume, and therefore an approximation of the particles, during friction, far from considerable, may evolve a large quantity of heat; and in some late experiments, he has shewn that the production of heat by percussion is attended with condensation, the density of a piece of metal struck forcibly in the coining press being increased, and the increase being greater as the metal gives out more heat. He has also shewn, what is in conformity to the same view, that a greater production of heat takes place from the first stroke than the second, and a greater from the second than the third, and after the third the rise of temperature is very inconsiderable, leading therefore to the conclusion, that there are limits to the production of heat by percussion.

The conveyance of caloric through a vacuum has been advanced as a proof of its existence as a material principle; but no perfect vacuum can be formed, and the proof therefore is defective. The phenomena of radiant caloric appear to demonstrate the existence of a subtle matter projected in right lines from heated bodies, capable of exciting temperature; and this would afford a conclusive proof of its materiality, were it unequivocally established that these phenomena are wholly independent of the air: on this point the speculations of Mr Leslie leave some doubt. The existence of calorific rays in the solar beam might be considered as affording similar evidence; but the degree of uncertainty under which the fact still remains with regard to this and to the relation of these rays to light, leaves an equal uncertainty as to the force of the conclusion. Though the hypothesis, therefore, of the materiality of ca-



loric, is superior in its adaptation to the phenomena to that which assigns the production of these phenomena to motion of the particles of matter, it can scarcely be considered as fully established.

It may be added, that those who have denied the materiality of this power, have limited the discussion, by embracing the hypothesis of Bacon, that the heated state of bodies arises from vibration of their particles,—an hypothesis which gives no adequate explanation. The question need not be considered under this restricted view. Caloric, if its materiality be not admitted, may be considered as a general force producing repulsion; and if we set aside the facts with regard to its apparent radiation, this would not be the most improbable opinion on the nature of this power. Our knowledge, however, is not sufficiently advanced on this subject, and, in particular, while the relations of caloric to light and to electricity remain imperfectly developed, and the nature of these agents is unknown, any hypothesis must rest on imperfect grounds.

The question with regard to the materiality of caloric has been attempted to be determined, by discovering if it is subject to gravitation, or has weight. The investigation has given rise to very discordant results, some experiments appearing to establish its gravity, others favouring even the opposite conclusion, that it counteracts gravitation, and, communicated to bodies, renders them positively lighter. These differences arise from the difficulties attending the experiments; and from the subtilty of this agent, it is not to be expected, even if it were subject to gravitation, that this could be discovered by any apparatus we can employ. We might probably as well attempt to weigh the particles of light. In some of the experiments,

accordingly, made with the greatest care, and with the most delicate apparatus, no sensible difference in weight in a body could be discovered when caloric was communicated to it, and when it was withdrawn.

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SECT. VIII.—*Of the Sources of Variations of Temperature, and the Applications of these to Practical Chemistry.*

THE tendency of caloric being to diffuse itself over matter, until an equilibrium of temperature is established, this would at length be attained, did no external causes operate by which it is counteracted. Such uniformity of temperature, however, would be incompatible with the varied operations of nature; it is therefore prevented by certain general arrangements, constant in their action, giving rise to, and limiting at the same time that extent of variation which these operations require.

The great source of natural heat is the action of the solar rays. As every part of the earth's surface is not equally, and at all times exposed to this action, inequality of temperature, giving rise to variety of climate, and change of season, must be established. The extreme of heat, however, which might accumulate where the action of the solar rays is most powerful, is preserved within due limits by changes to which the operation of this heat itself gives rise, and which, so perfect is this adjustment, are even rendered subservient to moderating cold, where it might become intense.

These important effects are obtained, principally from changes in the atmosphere, and in the distribution of wa-

ter. When the surface of the earth is heated, a portion of this heat being communicated to the air incumbent on it, this is expanded, and of course ascends; an ascending current is established, which is supplied by colder and more dense air pressed from every side; the accumulation of heat is retarded, and the warmer air, propelled to colder climates, gradually gives out the heat it had received. The agency of water is scarcely less important. As the temperature is elevated, it evaporates in greater quantity, and in passing into vapour absorbs caloric, from its increasing capacity, without rising in temperature: when the heat diminishes, or the vapour is carried to colder regions, it is condensed, and this latent caloric is rendered sensible. Where the cold becomes more intense, water is congealed, and in the congelation gives out the large portion of latent caloric peculiar to it in the liquid form: at the return of warmth, the ice is melted, and caloric is absorbed. The transitions of seasons are thus moderated, sudden and extreme variations guarded against, and the temperature of the globe is every where preserved more uniform.

The range of natural temperature is comparatively moderate, extending only from a few degrees above 100 of Fahrenheit to about 50 below the commencement of the scale. In tropical climates, the heat in the shade rises occasionally to 110°. In the north of Asia and of America, the cold, in the winter season, is sufficiently intense to freeze quicksilver, and must therefore be lower than —40; the spirit thermometer has been observed to indicate —50, and there is no reason to believe that any natural cold much exceeds this. The mean natural temperature is about 50° of Fahrenheit.

The range of temperature as excited by artificial methods is much greater. We cannot indeed exceed greatly the greatest natural cold, the reduction of temperature by the most powerful freezing mixtures not being more than  $-100$ , or  $132^{\circ}$  below the freezing point of water. But our power of exciting heat is less restricted; it has been measured so high as  $160^{\circ}$  of Wedgwood's pyrometrical scale, or  $21,877^{\circ}$  of Fahrenheit; and as at this temperature effects were not produced, which can be obtained from the concentration of the solar rays by a powerful lens or speculum, or by the heat excited by a current of oxygen gas directed on burning charcoal, heats more intense than this are of course under our command.

An important subject in practical chemistry, is that which relates to the processes for obtaining and applying artificial heat and cold. An account of these, with a description of the apparatus adapted to them, concludes the chemical history of caloric.

The sources of heat are, the Solar rays, Electricity and Galvanism, Condensation, Mechanical action between solids, including Friction and Percussion, and, lastly, Chemical action, to which Combustion belongs.

From the action of the solar rays without concentration, the thermometer is raised to above  $100$ , and when protected from a current of air, even to above  $200$ . When concentrated by a lens or mirror, the heat is of extreme intensity, equal perhaps to any that can be excited by artificial arrangement, all the metals and earths nearly being melted by it, and many of them even dissipated in vapour. It admits, however, of very limited application, owing to

the smallness of the quantity of matter on which it can be made to operate.

The electric spark produces heat sufficient to kindle a combustible body, and the discharge from a battery raises the temperature of the matter through which it is transmitted to a degree more or less intense, according to the strength of the discharge. The galvanic discharge, which is merely a different form of electricity, produces heat still more intense, melting the most refractory of the metals, causing all of them to burn, dissipating them in vapour, and fusing the earths.

The effect of condensation in producing heat is most conspicuous in the compression or rarefaction of elastic fluids, as in these a considerable change of volume can be suddenly produced. By condensing a gas, its temperature is raised; and by a forcible and rapid condensation, this extends even to the temperature of ignition, a piece of tinder being kindled by condensing the air in a metallic tube. In rarefying any elastic fluid, cold is always produced.

Friction and Percussion are well-known sources of heat. Two solid bodies rubbed against each other become warm, and frequently so much so, that if inflammable they are kindled; the heat excited varies according to the hardness, elasticity, and other qualities of the body; the hardest are not those that are most heated. Of heat from percussion, the spark struck by steel from a flint is a familiar example, in which the temperature is raised to ignition.

Chemical action is perhaps invariably attended with a change of temperature; it is often productive of heat, and in some cases in a state of high intensity. Combustion is an example of this, this process being the combination of

one of the aerial ingredients of the atmosphere, oxygen gas, with the combustible body, and the heat produced arising directly from this combination. It is therefore much regulated by the rapidity with which the combination is effected.

If oxygen gas, in its pure form, be supplied to the combustible matter, the combustion is rapid; and the heat is therefore intense; and by this method; indeed, we obtain degrees of heat as high as appear to be capable of being excited by artificial arrangements. The oxygen gas is either directed in a stream on ignited charcoal, or a current of it is mingled with a current of an inflammable elastic fluid, hydrogen, and the mixed gases are kindled.

In exciting combustion, merely by supplying atmospheric air to the burning body, it is accelerated, and of course the heat is increased by certain arrangements, causing the air to be more freely and rapidly supplied. On this principle, in particular, is founded the construction of furnaces; a kind of apparatus extensively employed in chemical experiments, as applying heat.

The essential parts common to every furnace, are the body or fire place in which the fuel burns, and where the vessel containing the materials to be operated on is placed, —the chimney by which the smoke and heated air escape, —and the ash-pit designed to receive the ashes of the fuel, and by apertures in which air is admitted to regulate the combustion. The advantage from an apparatus of this kind in exciting combustion, is derived from its causing a more rapid circulation of air. The air in the upper part of the furnace is rarefied by the burning fuel; it therefore ascends by the chimney, and colder air entering from beneath, rises through the interstices of the fuel, and produ-

ces a combustion more rapid as it is more freely supplied. From this it is evident, that the higher the chimney is, (at least to the extent of the air within it not being much cooled,) the more rapid the current of air will be, for the difference will be greater between the specific gravity of the column of heated air, and the corresponding column of the external atmosphere, and the pressure by which the air is forced in at the bottom will be greater. On this principally depends the power of the furnace to produce intensity of heat.

It is necessary, too, to confine the heat and prevent its dissipation. This is accomplished by coating the inner surface with some substance which transmits heat slowly, as a lute of clay and sand, which also serves to defend the furnace, when constructed of metal, from the action of the fire. When fixed, and built of brick, the building is a sufficiently imperfect conductor to confine the heat.

A very convenient general furnace, applicable to most of the operations of chemistry, was contrived by Dr Black. It is represented Plate II. Fig. 11. A is the body of the furnace, of an elliptical form, which contains the fuel, and frequently the substance to be operated on, made of plate-iron, and lined to the thickness of two or three inches, first with a mixture of clay and charcoal, beat into a paste with water, and over this, next to the fuel, with a coating of clay and sand. On the top of the body is fixed an iron-plate, having two apertures, one, *a*, placed over the cavity, and designed to receive an iron-pot with sand, the other smaller, to which the chimney, B, made of a tube of iron, is fixed. C represents the grate, in a plate of iron which is fixed to the bottom of the body of the furnace, nearly, but not exactly opposite to the larger aperture in the up-

per plate. D is the ash-pit, the body of the furnace being received into it, and resting on a strong ring round the cavity, at about half an inch deep. In this ash-pit are a door, *b*, turning on hinges, by which the ashes may be removed; and a register, *c*, designed to regulate the admission of air. The register is a plate of iron, in which are six apertures, filled with plugs; the size of them increasing in geometrical ratio, so that by opening them singly, or in combination, the supply of air to pass through the fuel, and consequently the heat to be excited in the furnace, can be regulated with precision. The fuel is introduced at the top, but as it cannot easily be supplied this way in the progress of the process going on in the furnace, at least when the sand-pot is used, the furnace is sometimes constructed with a door in the side, though this renders the regulation of the admission of air less perfect. When the furnace is used for fusion, or similar purposes where a sand-pot is not required, the upper aperture is covered with a dome.

In operations on a larger scale, a fixed furnace of brick, and capable of exciting an intense heat, is required. Fig. 12. represents the usual form of a melting furnace of this kind, the structure of which is obvious from the figure. A is the cavity of the furnace, terminating by a passage in the chimney B, which is raised to the requisite height. At C is an aperture covered with a plate of iron, or of fire-brick, through which fuel is introduced. On the grate, D, is placed a covered crucible, on a pedestal of baked clay; and in the passage of the chimney, at *a*, a muffle is sometimes placed; E is the ash-pit, through which the air is admitted to the fuel.

When solid substances are to be exposed to these intense heats to fuse them, or to favour their mutual chemi-



cal action, crucibles of baked clay, or of clay with an intermixture of the mineral substance named plumbago or black lead, are the vessels generally employed, for experimental purposes. The usual form is represented Fig. 13. Crucibles of platina are sometimes used. Cupels are small cups made of bone-ashes, very porous: they are used principally in refining the more precious metals, the vitrified matter being absorbed by the cupel. They are placed under an arched earthen vessel, open at the end, named a Muffle, Fig. 14., by which, while the fuel is excluded, the air which is necessary in the process is freely admitted.

In applying a more moderate and equable heat to favour chemical action, the medium of sand, forming the Sand Bath, is generally employed, and glass vessels named Matrasses or Cucurbits are used. The cucurbit is represented, with the alembic, Pl. III. Fig. 18. as the apparatus which is used in sublimation. The matrass is represented Fig. 9. Pl. II.: from being blown thin and equable, it sustains alternations of temperature with less risk of breaking, and from the length of its neck any vapour which is formed is condensed and falls back.

A convenient method of applying heat from combustion, where it is not necessary that it should be very intense, is by the Lamp-furnace. A lamp with a concentric wick, and internal supply of air, on the principle of Argand's, affords a heat which has the advantage of being easily regulated; the elevation or depression of the wick, and the distance at which it may be placed from the body designed to be heated, allowing the application of various degrees of heat, and their speedy change. By having a double circular wick, the heat is rendered more powerful, at least three

times more so than when the lamp with a single wick is used.

The lamp is sometimes attached to an iron or brass rod, on which it slides, and to which are attached rings of different diameters, to support a retort or matrass above the flame, as is represented Pl. I. Fig. 6.

A mode of applying a very strong heat at a small point, is that by the Blow-pipe. This instrument is a conical tube, with a small aperture at its narrow extremity, and having towards that extremity a moderate curvature. It is made of brass, or of glass. By blowing through this tube on the flame of a candle or lamp, in a horizontal direction, the flame is urged in a conical form, and at the extremity of it, or rather at the extremity of an internal blue flame, which is surrounded by one of white light, a heat comparatively intense is excited. It is used to ascertain the fusibilities of bodies, and by the artists, in enamelling and in working on glass, which is melted by it, so as to be capable of being moulded into any shape, or blow into vessels of a small size.

The facility of blowing through the blow-pipe, so as to keep up a constant stream of air, is not easily acquired, and it is fatiguing to continue it for any length of time. Different contrivances have been employed to obviate this inconvenience. The instrument is sometimes connected by a flexible tube with double bellows worked by the foot, by which a uniform stream of air is forced through the tube. The vapour of spirit of wine has been applied to the same purpose: a quantity of spirit being put into a small vessel which is heated over the flame of a lamp; and the vapour conducted through a curved tube is directed on the

flame of a candle, or that of a wick placed in a different part of the same tin lamp as that by which the spirit is heated. A valve is adapted to the vessel containing the spirit, to render the flame more regular.

The sources of Cold are Rarefaction, Evaporation, and Chemical Action.

The operation of the first is scarcely conspicuous but in elastic substances, as in these only can the volume be suddenly changed to any considerable extent. When a gas is rarefied by removing pressure from it, its temperature always falls, and the more sudden and great the rarefaction is, the cold produced is greater. By allowing air, previously compressed, to expand suddenly, the temperature is reduced below  $32^{\circ}$ ; and by the condensed air being previously cooled, more intense cold is obtained.

In the transition of substances to the aërial form, an augmentation of capacity always happens, whence an absorption of caloric follows. Evaporation, therefore, is attended with cold, which is greater according as the liquid passes more quickly into the aërial form, or as this is accelerated by circumstances. Thus, the bulb of a thermometer being moistened with water, and the evaporation being promoted by directing a current of air on it, the temperature falls 5 degrees, with alcohol under the same circumstances 12 degrees, and with sulphuric ether 30 degrees. Water therefore is easily frozen by cold produced by the evaporation of ether. On removing the pressure of the atmosphere, the evaporation is more rapid, and the cold is greater. In this way quicksilver may be frozen by the cold from the evaporation of ether. Or, if the evaporation go on in a receiver which has been exhausted of air, if an arrangement be at the same time introduced, by which the vapour from

the evaporating liquid is quickly condensed, the evaporation is more rapid and the cold greater. Mr Leslie first made this arrangement. by exposing water to evaporate in a receiver exhausted by the air-pump, and at the same time causing the absorption of the vapour by sulphuric acid placed in a wide vessel without the receiver, he succeeded in producing a cold sufficient to convert a portion of the water into ice. By coating the bulb of a mercurial thermometer with ice, and submitting it in a similar manner to the action of sulphuric acid in the vacuum of a powerful air pump, he succeeded in producing a degree of cold sufficient to freeze the mercury. Another arrangement on the same principle is that since constructed by Dr Wollaston; two glass balls being blown at the extremities of a tube eight or ten inches in length, and bent at both extremities at right angles immediately above the balls; one of the balls is half filled with water, which is made to boil to expel the air; the opening which has been left in the other ball is then hermetically sealed. If the empty ball be surrounded with a freezing mixture to condense the aqueous vapour, the evaporation from the water in the other ball is so rapid as to produce cold sufficient to freeze it.

Chemical action is a source of cold, by the rapid change of form to which it gives rise, solid substances, by combining, passing into the liquid form, and this being attended with enlargement of capacity.

The most simple example of this, is in the solution of a salt in water, which is always attended with a fall of temperature, in some cases to the extent of 20, 30, or 40 degrees. When mixtures of salt are dissolved, the reduction is still greater, and these form what are usually named Freezing Mixtures. Equal parts of muriate of ammonia, and of nitre in powder, added to water in the proportion

of 5 parts to 3, reduces the temperature from  $50^{\circ}$  to  $11^{\circ}$ , and this forms one of the most economical of these mixtures, as the solid matter recovered by evaporation, and dried, answers equally well as before.

By dissolving salts in acids more or less diluted, greater degrees of cold are obtained. Sulphate of soda, added to sulphuric acid, previously diluted with an equal weight of water, depresses the temperature from  $50^{\circ}$  to  $5^{\circ}$ . Mixtures of salts cause a greater depression. From phosphate of soda, and nitrate of ammonia, added to diluted nitric acid, a reduction is obtained from 50 to  $-41$ .

The cold from similar actions exerted between these substances, and ice or snow, is still more intense; as the absorption of caloric from the liquefaction of the ice is added to that from the solution of the saline matter. Acids, in a certain state of dilution, poured on snow or ice, reduce the temperature to 10, 20, or 30 degrees below the freezing point of water. Solid salts mixed with snow are often equally powerful. A mixture of common salt and snow, afforded Fahrenheit the temperature at which he commenced his scale. A mixture of dry potash and snow reduces the temperature to  $-53^{\circ}$ , and a mixture of muriate of lime and snow to  $-56^{\circ}$ .

From the application of these freezing mixtures, the effects of intense cold on a number of substances have been ascertained. Quicksilver is easily rendered solid; the most ductile of the metals lose their ductility; liquids that resist freezing most powerfully, as wines, brandy, ether, and nitrous acid, are congealed; and some of the gases that appear permanent, as ammonia, and oxy-muriatic acid gas, have been brought to the liquid form. Alcohol highly rectified is the only liquid that had resisted the congealing

power of these mixtures: it has lately been frozen by Mr Hutton by a method not made public, but which must of course produce very intense cold.

The process of artificial refrigeration, to be successful, requires to be conducted with attention to several circumstances. The solid salts ought to be recently crystallized, dry, and reduced to fine powder, the due proportions observed, the materials accurately mixed, the vessel employed an imperfect conductor, the air excluded as much as possible, and, to attain extreme cold, the materials must be previously cooled, taking care only not to cool them below that temperature at which they can act on each other.

The theory of the action of freezing mixtures ultimately rests on the principle, that the reduction of temperature arises from the augmentation of capacity, produced by the rapid liquefaction of the solid ingredients. There are some general facts, however, connected with this, of importance, particularly as enabling us to point out what substances are best fitted by their mutual action to produce cold, what degree of cold may be expected from their mixture, what will be the maximum of refrigeration, and what the best proportions of the materials.

It is obvious, that those substances will produce the greatest cold, which, by their mutual action, produce the most rapid solution,—which, during that solution, suffer the greatest augmentation of capacity,—and which form a compound that at low temperatures remains liquid. There is perhaps no individual mixture in which all these circumstances are present to the greatest extent; yet the knowledge of them enables us to point out the respective powers of the mixtures usually employed.

Thus, in the solution of a salt in water, there is merely

the gradual transition of the solid to the fluid form; hence the cold produced is not considerable. When two salts are mingled together, these, by their reciprocal action, both accelerate the solution of each other, and enable a given quantity of water to dissolve a greater quantity: as more solid matter, therefore, passes to the liquid state, and does so more quickly, a greater portion of caloric is absorbed in a given time, and a greater degree of cold is produced. The attraction of acids to water, or rather to the solid matter of water, is strong, and their mutual action energetic; ice too is a substance which, in its transition to fluidity, suffers a large augmentation of capacity; hence it may be concluded, what experiment proves to be just, that from the action of acids on snow or ice, a great degree of cold will arise. In the mixture of two solid substances, which by mutual action pass to fluidity, the comparative enlargement of capacity must be still greater, and a greater diminution of temperature produced, though this is in some measure limited by the greater slowness with which two solids act on each other.

Another principle is to be attended to, which in these mixtures modifies the quantity of caloric absorbed from the liquefaction. Although the indirect consequence of the chemical action between the substances mixed is absorption of caloric, in consequence of the liquefaction it occasions, yet its direct tendency is to evolve caloric, by the increase of density which chemical action, independent of change of form, occasions. Hence two effects result from the mutual action of the ingredients of freezing mixtures,—evolution of caloric, as the immediate result of the combination, and absorption of caloric, as the result of the liquefaction to which the combination gives rise; and the ultimate ef-

fect is compounded of these, or the actual change of temperature is only the excess of the one over the other. This is generally cold, but the reverse sometimes happens, as in pouring a concentrated acid on snow, or dissolving solid potash in water; and where cold is produced, it is always lessened by this cause. It is therefore sometimes advantageous to diminish the energy of the more active substance by previous dilution, as in employing the acids; and in all cases there is a certain state of concentration of the materials, and a certain proportion of them, from which the greatest cold will be obtained.

Lastly, it is to be remarked, that we do not obtain the reduction of temperature to the lowest point in the thermometrical scale from those mixtures which, during their mutual action, absorb most caloric. If we take two freezing mixtures at  $32^{\circ}$ , the one muriate of lime, and snow, the other diluted sulphuric acid and snow, the former will produce more cold than the latter; it will sink the thermometer to  $-40^{\circ}$  or  $-50^{\circ}$ , while the other will sink it to not more than  $-25^{\circ}$ . But we may reach a lower point in the scale of temperature, by successive application of diluted sulphuric acid and snow, than we can do by muriate of lime and snow; for, past a certain temperature, the latter mixture does not liquefy, but, on the contrary, were it liquid would become solid, while the former remains liquid at lower temperatures than this. If we cool, for example, previous to mixture, muriate of lime and snow to  $-73^{\circ}$ , no advantage is gained; we even rather diminish their mutual action, by adding to the cohesion of each. But, by previously cooling diluted sulphuric acid and snow, an important advantage is gained; the same limit is not placed to their mutual action, and the lower the tempera-



ture is reduced, the lower will the temperature be that results from that action, down to the point at which the liquid formed by the action of the acid on the snow would congeal, and this is much lower than in the other.

This furnishes us therefore with the general rule, that the temperature can never be reduced by a freezing mixture beyond that point at which the liquid combination resulting from that mixture congeals or crystallizes, and must indeed always be a degree or two above it. It also, in some measure, determines the proportions in which the substances should be mixed together; those being best, in which the action shall be most rapid, without being too energetic to evolve heat from the combination, and in which the resulting solution is of that strength, that is least liable to congeal or crystallize.

In the Appendix will be found a table of these freezing mixtures, which are preferable, either as being economical; easily managed; or capable of producing very intense colds.

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## CHAP. II.

### OF LIGHT.

**T**HE materiality of Light, and its insulated existence, are sufficiently demonstrated. Its emission from bodies, its motion even to the most distant regions of space independent of any medium, the changes which may be produced in that motion by reflection and inflection, and the chemical effects it produces, are proofs of this material existence, free from all doubt. We cannot easily, however, trace the combinations of light: we observe only its evolution and absorption, and the effects arising from these, without being able to discover how far it influences the constitution of bodies in which it exists, or to what extent it is liable to the laws of chemical attraction. Its chemical history, therefore, falls to be considered under a point of view nearly the same as that under which caloric is regarded. And with that power it may justly be associated as a repulsive agent, the particles of light being mutually repellent, and operating perhaps as much in the production of chemical changes by the repulsion they communicate, as by the affinities they exert.

Light has been regarded as consisting of particles of extreme minuteness, projected from luminous bodies, and moving in right lines with the utmost velocity. It has also been considered as a continuous fluid of perfect elasticity and extreme tenuity, diffused through space, in

which vibrations are excited by luminous bodies, so as to produce its peculiar phenomena. The former opinion has been more generally received, as better adapted than the other to the explanation of the physical affections and relations of light; and it appears to be more directly established by the chemical agencies of this power,—its absorption by bodies, and its subsequent evolution. If it be admitted, the minuteness of the particles of light must be extremely great, beyond even what the imagination can clearly conceive, as is evident from the velocity of their motion, and their not being interrupted, though moving in space through which innumerable rays are constantly projected.

The particles of light are mutually repellent. So perfect is its elasticity, that it is reflected from a body at an angle equal to the angle of its incidence. It is subject to the attraction exerted between masses of matter, as is proved by the inflection it suffers in passing near to any body, or in passing obliquely from one medium into another, which gives rise to its refraction.

A ray of light is not homogeneous, but consists of particles suffering refraction in different degrees, and hence capable of being separated. These excite the sensation of vision under different modifications, giving rise to different colours; they also produce different chemical effects. An entire ray of light is, by transmission through a triangular glass prism, divided into seven rays, the red, orange, yellow, green, blue, indigo and violet, the red being the least refrangible, and therefore falling on a space least distant from that on which the undivided ray would have impinged, had its direction not been changed; the violet being the most refrangible, and falling therefore on

a space most distant from this ; the others being arranged between these, the whole forming the prismatic spectrum. In this the different coloured rays occupy unequal spaces, and their limits are not perfectly defined. The differences in the properties of the coloured rays have been supposed to depend on the different magnitudes of their particles, or on the different velocities with which they move,—suppositions which, however they may be adapted to the physical relations of these rays, scarcely explain the differences in their chemical powers.

Light is differently affected by different bodies. It passes through some with little interruption ; by others it is reflected ; some reflect one ray retaining the others,—an effect giving rise to the colours which bodies exhibit : there are, lastly, some in which the light is absorbed, and is lost by numerous reflections and refractions.

Light forms a more intimate union with bodies, of which there are different degrees. By some it is absorbed, and is again slowly emitted without any sensible change : in others it occasions alterations of temperature, or of composition, acting as an important chemical power.

The property which has been named Phosphorescence, appears to depend on the first of these kinds of combinations. There are a number of substances which, when exposed to light, appear luminous when removed from it, and continue so for a longer or shorter time. These are named Solar Phosphori, and the luminous appearance in them appears to arise from the light being imbibed, and again slowly emitted.

This property is conspicuous in a number of natural substances, particularly in earthy minerals, as the gems, marble, heavy spar, fluor spar, and others ; and also in

bodies belonging to the vegetable and animal kingdoms, as in sugar, paper, the shells of marine animals, &c. Solar phosphori can be prepared by artificial processes still more powerful. The Bolognian phosphorus, in which the property was first observed, is prepared from sulphate of barytes made into a paste with mucilage, and calcined in contact with ignited charcoal. Canton's phosphorus, which is still more powerful, is formed from calcined oyster shells, mixed with sulphur, and exposed to the heat of ignition in a crucible for an hour.

There is much diversity in the degree of phosphorescence. Some, even after exposure to solar light, shine so feebly, that the eye requires to be rendered sensible by previous darkness to perceive it. Others are illuminated by the mere light of day; and some become phosphorescent when exposed to the light of a lamp. Some are rendered luminous by an electrical discharge. The light emitted is not always white; it is frequently yellow or red, and some phosphori exhibit the prismatic colours.

Temperature has a marked effect on the emission of light by these bodies. When they are shining, the luminous appearance ceases if they are exposed to the cold of a freezing mixture. It becomes more vivid by applying heat; and if it has ceased, it may be renewed by applying a stronger heat, so that a piece which has been for some time quite dark, may be made to shine. When the phosphorescence, however, has been excited by heat, it ceases proportionally sooner, and is not renewed but by exposure again to light.

This property is quite independent of the action of the air; a phosphorescent substance shining clearly when inclosed in a mass of glass.

The phenomena of solar phosphorescence appear to lead to the conclusion, that light is absorbed by the phosphorescent body, and is again emitted, this emission being promoted by the repulsive agency of heat. There is an objection, however, to this in the fact, which appears to be sufficiently established, that, in exposing the phosphorescent body to a particular coloured ray, it is not this coloured light it emits, but merely the light which usually proceeds from it; one which shines with a white light continuing to do so, whatever ray of the spectrum it has been exposed to; or one which usually exhibits the prismatic colours when rendered luminous, still doing so whether it has been submitted to white light, or to the coloured light of any individual ray. These facts are singular, and not easily explained on any theory; but it is not impossible that one species of coloured light may be capable of being converted into the others,—a supposition which would, in some measure, reconcile them with the obvious theory of phosphorescence.

Another species of phosphorescence is that excited by heat, independent of any previous exposure to light, and which is incapable of being renewed. It is exhibited particularly by fluor spar, by several of the gems, and by a number of earthy fossils, the luminous appearance being more or less vivid when heat is applied. The light emitted is often coloured; that from fluor spar is purple; in some the luminous appearance is momentary, in others it continues longer; it is equally, with the former, independent of any action of the air.

Phosphorescence, apparently similar to this, is excited by attrition; two pieces of quartz, for example, appearing luminous in the dark when rubbed against each other, and

other fossils shining even from very slight friction. From some the light is colourless, from others coloured : its production is independent of any action of the air, as it is equally bright under water ; it is not accompanied with any signs of electrical excitation. The attrition might be supposed to excite the light by the heat it may produce ; but the very slight friction that is often sufficient to produce the luminous appearance, is unfavourable to this opinion : there are fossils, too, rendered phosphorescent by friction and not by heat, and *vice versa* ; and in those which are phosphorescent from both causes, if the luminous appearance has been excited by heat until it cease to appear, it may be produced anew by attrition.

A kind of phosphorescence, different from any of the preceding varieties, is that exhibited by animal matter. Marine animals are remarkable for this property ; almost all the species of sea fish becoming luminous after they have been removed for some time from the water, and continuing to shine for some days. The same appearance has been occasionally observed from the flesh of quadrupeds. It does not appear until the animal has been for some time deprived of life, but it is always apparent before there are any signs of putrefaction, and it ceases when that process is fully established.

The most important fact with regard to this species of phosphorescence is, that the matter having the luminous quality can be extracted in a state of solution. If the substance of any marine animal in the phosphorescent state be macerated in a saline solution, as that of sea-salt, or any other neutral salt of a certain strength, a lucid ring soon appears at the surface, and the whole becomes luminous when agitated ; this continues for several days, becoming

gradually more faint until it is extinguished. Fresh water is incapable of extracting this luminous matter; the luminous appearance in salt water is extinguished by acids, alkalis, ardent spirit, and other substances. A certain degree, too, of saline impregnation is necessary to its appearance; for it is suspended by a solution either too dilute or too concentrated, being revived in this case when the proper state of concentration is restored.

This phosphorescence is augmented by agitation: it is impaired and even extinguished by cold, but is revived by heat: if the heat, however, be too high, such as that of boiling water, it is irrecoverably extinguished. Exclusion from the atmosphere prevents its appearance, and a number of elastic fluids not only prevent it from appearing, but extinguish it when it has been produced. It is not brighter, however, in oxygen gas than in atmospheric air; neither is it accompanied with any sensible heat.

The light from rotten wood appears to be of a similar kind, observing, in its production and extinction, very nearly the same relations.

Light is emitted from certain insects, as from the glow-worm, or the lantern-fly: the light is variable, being at one moment brilliant, at another faint. The luminous appearance depends on a peculiar secretion, and may even be obtained from its receptacle by compression; it continues to shine, too, for some time after the death of the animal. It had been observed, that the light of the glow-worm becomes more vivid when it is placed in oxygen gas, which gave rise to the suspicion of its being produced by the chemical action of oxygen. The gas, however, appears to act rather by exciting the secretion, for the oxygen is not impaired in purity; and the luminous appearance is obtained when the animal is under water. This species of



phosphorescence, like that from marine animal matter, is extinguished by hydrogen, carbonic acid, and other elastic fluids, but revives on admitting atmospheric air.

An important part of the chemical history of light relates to its power of elevating temperature. The solar rays are the great source of natural heat; and when concentrated, excite a very intense heat.

Different kinds of matter are unequally heated by solar light; through transparent bodies the rays passing with little interruption, the temperature is not so much raised as in those which are opaque, and those which are white are less heated than those of a darker shade.

A still more important fact connected with this property is, that the different coloured rays of light have different heating powers. Hutton observed, that the red ray of light has more heating power than white light. Rochon found that an air thermometer, exposed successively to the action of the different coloured rays, separated by a prism, rose higher, as it was moved from the violet to the red, the difference in the two extremes being nearly 8 to 1. Herschel and Englefield have demonstrated the same general fact, and shown the relative heating powers of the coloured rays with more precision. The rise of a delicate mercurial thermometer placed in the focus of a lens, and exposed successively to the coloured rays obtained by a prism, is shown in the following table given by Englefield.

|                            |       |      |            |
|----------------------------|-------|------|------------|
| In the blue-ray            | in 3' | from | 55° to 56° |
| In the green-ray           | in 3  | from | 54. to 56. |
| In the yellow-ray          | in 3  | from | 56. to 62  |
| In the full red-ray        | in 3½ | from | 56 to 72   |
| In the confines of the red | 2½    | from | 58 to 73½  |
| Quite out of visible light | 2½    | from | 61 to 79   |

From the last number in the table, indicating a high degree of heat to be produced quite beyond the visible rays, the important result appears to be established ; that there exist in the solar beam invisible rays which are powerful in producing heat, these being accumulated beyond the red ray when the entire beam has been decomposed by the prism, and being, of course, less refrangible than the red ray. This had been previously shewn by the experiments of Herschel. Exposing a thermometer to the different rays of the prismatic spectrum, each ray being allowed to pass successively through a piece of pasteboard with a slit in it, so as to exclude the others, he found not only that the heat increased progressively from the violet to the red ray, but that when the aperture in the pasteboard was brought to coincide with the space beyond the red ray, the heat continued: it was even greater at the distance of half an inch than in the red ray itself, and is here at its maximum ; at the distance of an inch, the rise of the thermometer amounted to  $5\frac{1}{4}^{\circ}$ , being 7 in the red ray, and the heating power was sensible at the distance even of an inch and a half. Beyond the violet ray there is no sensible heat.

Admitting the accuracy of these experiments, it is established, that in the solar rays, there are invisible calorific rays, as well as visible rays of light. Now this being proved, the hypothesis may be proposed, that the apparent heating power of the visible rays of light is not a property belonging to them, but depends on the presence of calorific rays associated with them. The entire beam of visible light is not homogeneous, but consists of rays, which, being of unequal refrangibility, are capable of being separated, forming, when thus refracted, the visible or coloured spectrum. The calorific matter in the solar beam, it is equally

probable, may not be homogeneous, but may consist of rays of different refrangibility. If so, these rays will also be separated by the prism, and an invisible calorific spectrum be formed, the rays composing which may differ in heating, as the rays of light differ in illuminating power. If this happen, the one spectrum will be in some measure blended with the other, and thus the visible rays of light will appear to have different degrees of heating power, though in themselves they may have no power whatever to produce heat.

Herschel endeavoured to establish this conclusion, by experiments resting on the following assumption : Taking the illuminating power as the property characteristic of visible light, if the heating power of any ray be a property belonging to it, and not depending on any calorific ray associated with it, it seems obvious, that when the coloured ray is transmitted through a certain medium, as, for example, through glass, its illuminating and heating powers must be diminished exactly in the same proportion. It is not to be expected, that it will pass through without a certain degree of interruption ; but it may be presumed, and appears indeed to be a necessary inference, that if both properties depend on the same matter, they must be diminished to the same extent, while, if the illuminating power depends on one kind of ray, the heating power on another, it is possible, *a priori*, and indeed to be expected, that these will be unequally intercepted, and of course the powers will be unequally impaired.

To ascertain the fact with regard to this, a very extensive series of experiments was executed by Herschel, and the general result established, that the two powers, that of illumination, and that of heat, are very unequally impaired.

ed by transmission of light, either entire, or in the state of the different coloured rays through transparent media. It appeared therefore to follow, that the two properties do not depend on the same agent: the illumination depends on rays of light, the heat on calorific rays: and in any coloured ray the two properties appear together merely because from the correspondence in the order of refrangibility, certain of the calorific rays are associated with certain of the visible rays of light. Herschel has pointed out some other results in comparing their properties, which strengthen the conclusion; the interruption, for example, of the rays of heat becomes less, as its transmission is continued; while this does not happen with regard to light: and the effect of rough surfaces in scattering the rays of light being much greater than it is on the rays of heat.

The experiments on the calorific rays of the solar ray have been lately repeated by Berard, with an apparatus which, giving a coloured spectrum perfectly stable, admitted of their powers being determined with great precision. The results confirm those of Herschel, that the heating power increases progressively from the violet to the red; but differ in this, that the maximum is not beyond the coloured spectrum, but exactly at the boundary of it, where the bulb of the thermometer is entirely covered with the red ray. The effect, became less and less as the thermometer was moved out of the visible spectrum, and where Herschel had fixed the maximum, Berard found it to be only one-fifth of what it was in the red ray. The absolute intensity of heat produced was also less than in the experiments of Herschel. Part of these differences, as Berthollet suggests, may arise from diversity in the materials of the prism, or other circumstances of the experi-

ment. The calorific rays Barard found to be liable to the same effects as the visible rays; its transmission through a medium producing double refraction; in reflection, and in being polarized. It is also liable to the same effects as the visible rays in producing chemical decomposition. The agency of light in producing chemical decomposition still remains to be stated. The analysis of great numbers of compounds, and the changes of this nature produced by its action arising from the separation of the elements, especially from states of combination. And as this element enters into the constitution of an extensive series of compounds, a number of substances are changed by light exerting its depurating power. Thus, several of the acids are decomposed. If nitric acid, which is colourless, be exposed to the rays of the sun, it becomes of a yellow colour, and oxygen is distinguished from it. Oxymuriatic acid, under a similar exposure, likewise yields oxygen. A number of compounds of metals with oxygen, either alone, or in combination with acids forming metallic salts, undergo a similar decomposition: in some of them this is partial; in others as in the salts of gold or silver, it is complete, so that the metal returns to its metallic form. Some of these compounds are extremely sensible to the chemical agency of light: muriate of silver, for example, is darkened in its colour by the mere light of day, without direct exposure to the rays of the sun. The changes of metallic pigments from exposure, in general arise from this action of light.

The process of bleaching, too, depends chiefly on the chemical power of light; the colouring matter of the vegetable fibre apparently receiving oxygen from the decomposition by light of the water with which it is moistened.

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The changes which growing vegetables suffer under exposure to the solar light, display its power in modifying even by its chemical agency the processes of animated nature. If light is excluded, or very partially supplied, plants are in general feeble, of a pale colour, and do not afford their proper products fully formed : if it is freely admitted, they soon acquire a green colour and their natural vigour : those which grow under a clear sky and an intense solar light, are even in general more aromatic, and afford more rich and elaborated juices than those which grow under the opposite circumstances. With these results we can connect the usual chemical change from the action of light, oxygen being exhaled from plants while under exposure to the rays of the sun. Even on animals light perhaps exerts its chemical power : those who are natives of the arctic regions, being, like vegetables secluded from light, usually of a pale or white colour, while those who inhabit tropical countries are marked by deep or brilliant hues.

It might be supposed that these chemical effects depend not on any peculiar action of light, but arise from its power of exciting heat ; some of them being produced by an elevation of temperature. An experiment of Scheele's appears to set aside this supposition ; nitric acid, which becomes coloured when exposed to the sun's rays, not suffering this change when exposed to them in a phial painted black, though its temperature must have been more elevated than if it had been exposed in a clear phial. Berthollet also found, that oxymuriatic acid, exposed to solar light in a phial covered with black paper, did not suffer the usual change, though it must have been at least equally heated. But these experiments are not perfectly con-

clusive; for we cannot estimate correctly the heat produced by the solar rays from the elevation of temperature in the entire mass of matter exposed to them, as this may be moderate, while it may be intense in the minute points on which the rays impinge; and at these points it may, from its intensity, give rise to the decompositions which are produced. The hypothesis, however, that light acts in producing these decompositions by the heat it excites, is refuted by the fact to be immediately stated, that those rays most powerful in exciting heat, are least powerful in giving rise to chemical changes.

Light, it has been discovered, is equally powerful in promoting, with regard to some bodies, chemical combination. Gay-Lussac and Thenard, and Mr Dalton, observed about the same period, that a mixture of oxymuriatic gas with hydrogen gas suffers no change for a considerable time when light is excluded; they act on each other when it is admitted; and under exposure to the direct solar rays, the action is so rapid as to be accompanied with explosion. The effect in this case is probably owing to the usual decomposing agency of light favouring the decomposition of the oxymuriatic acid, and the transfer of its oxygen to the hydrogen.

The comparative powers of the different coloured rays in producing chemical decomposition, were submitted to experiment by Scheele; muriate of silver, the substance which is so rapidly affected by light, being exposed to their action; it became sooner black, he observed, in the violet ray than in any of the others. Sennebier ascertained the differences more minutely. The shade produced in the muriate of silver by exposure to the violet ray for 15 seconds, required for its production, exposure to the indi-

go ray 23 seconds; to the blue 29; the green 37; the yellow 54 minutes; the orange 12 minutes; and the red not less than 20 minutes. The blue ray too is superior to the others in exciting phosphorescence. According to Seebeck, the mixture of oxymuriatic gas and hydrogen is very slowly acted on when exposed to solar light, in a vessel of red coloured glass, while it is acted on very rapidly when exposed to the action of light transmitted through a blue glass.

The discovery of the existence of invisible calorific rays in the solar beam might suggest the conclusion, that there may also exist in it invisible chemical rays, to which the chemical powers of the visible rays is to be ascribed. Ritter submitted this conjecture to experiment. Placing muriate of silver without the coloured spectrum beyond the violet ray, it was blackened; while, on placing it beyond the red ray at the other extremity, it not only did not suffer this change, but if previously blackened became white. Phosphorus was kindled in the space beyond the red ray, but was extinguished when transferred to that beyond the violet. In the violet ray itself the muriate of silver received a less deep shade than in the space beyond it. Dr Wollaston had nearly about the same time made similar experiments, and with the same results, except that when the muriate of silver had been blackened, however slightly, it did not recover its whiteness from exposure to the red rays. Berard has repeated these experiments, and found, that the chemical or decomposing power of light increases towards the violet extremity of the spectrum, and extends to a small distance beyond it.

From these experiments, the existence in the solar beam of invisible rays not calorific, but distinguished by their



chemical action, and more refrangible than the visible rays of light, appears to be established. Reasoning by analogy from the law which exists with regard to the calorific rays, it might be concluded, that the matter composing what, for distinction, may be named the Chemical Rays, is not homogeneous, but consists of rays of different refrangibilities; that from this difference they are spread to a certain extent over the space occupied by the prismatic spectrum, and that, as the calorific effect of the visible rays does not belong to them, but to rays of caloric intermixed with them, so the chemical powers of these rays may not arise, strictly speaking, from the action of light, but from the action of chemical rays blended with the others. It has accordingly been affirmed, that Ritter, by transmitting the coloured rays through different prisms, has separated them from the chemical rays, and thus produced a coloured spectrum without any chemical power.

According to this view, three distinct species of rays exist in the solar beam, the visible rays of light, distinguished by their illuminating power; the invisible calorific rays, and the invisible chemical rays: and when passed through the prism, three spectrums are formed, blended together. It is certainly possible, however, that the three properties characterizing these may depend on the same agent; that, as suggested by Berthollet, light may consist of a collection of rays unequally refrangible; that those of a medium refrangibility may be best adapted to excite the sensation of vision; that others, more or less refrangible, may be less fit to produce this effect, and towards the extremes may be incapable of producing it, while, from the same cause as that producing their difference of refrangibility, they may be better adapted on the one hand to act

chemically, or on the other to excite heat. This more simple view is perhaps confirmed by all these rays observing, in their motion and other affections, nearly the same laws.

From the relation which subsists between light and caloric, it has sometimes been supposed that they are ultimately the same, or are modifications of one matter, light being this matter in a state of rapid projectile motion; and acting as caloric when it becomes quiescent. Though it may be difficult to explain fully the nature of that relation, there are important objections to this hypothesis. The essential properties of light, and particularly its chemical agencies, are very different from those of caloric,—differences which the hypothesis does not explain; more especially taking into consideration the important fact, that these chemical agencies are exerted most powerfully by those rays of light which are least powerful in producing heat. Neither is there any proof of the assumption, that caloric, in any state of motion, can assume the properties of light. Yet in the properties of radiant caloric there is no doubt an approximation to those of light; and the fact, that the rays projected from a body highly heated, penetrate transparent media with more facility than those emitted at a lower temperature; shews in some measure a gradation of properties from the radiant caloric of heated bodies to the calorific rays of the solar beam, and these again form a transition into the visible rays of light.

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### CHAP. III.

#### OF ELECTRICITY AND GALVANISM.

THE agent on which the phenomena of electricity depend, operates as a chemical power. There is every reason too to conclude, that the galvanic principle is merely electricity under a peculiar form, and in this form its chemical action is still more powerful, and indeed nearly unlimited. Under either form it is to be regarded as a repulsive agent, or force counteracting chemical attraction, and as such belongs to the same class as light and caloric, with which it is farther intimately connected in its power of raising temperature and of exciting illumination.

Though electricity and galvanism are modifications of the same power, yet, as their mode of excitation is different, and the chemical effects obtained from each are peculiar, they require to be considered apart.

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#### SECT. I.—*Of Electricity.*

CERTAIN bodies submitted to friction exhibit the phenomena denominated Electrical. A dry glass rod, for example, when rubbed with a piece of dry silk, will give sparks of light from its surface, and will first attract light bodies

and then repel them. These effects, however, are not obtained from the friction of every body; thus, a metallic rod does not exhibit them. Hence the distinction of bodies into *electric*, or those capable of being excited by friction, and *non-electric*, or those which are incapable of this electrical excitation.

If, when an electric has been excited, a non-electric be applied to it, the signs of electricity in the former instantly cease, while this does not happen from the application of an electric of a different kind. The electrical state may also be conveyed by this interposition of the non-electric to another body. Hence the origin of another distinction, that of Conductors, and Non-conductors of Electricity; the former affording a passage to the electrical principle, and carrying it off where it has been excited; the latter being impervious to it. Electrics are non-conductors; non-electrics are conductors; glass, resinous substances, oils, and sulphur, are the principal substances belonging to the first class; metals, water, liquid acids, saline solutions, and a number of earthy bodies belong to the other.

If an electric, when submitted to excitation, be supported on a non-conductor, the electricity it gives out is limited. But if a communication be established with the earth by the medium of a conductor, this conveys and supplies electricity as long as the exciting cause is applied. And if a conductor insulated, that is, placed on a non-conductor, be brought nearly in contact with the excited electric, it receives the electricity which is evolved, and retains it in an accumulated state. On these principles the electrical apparatus is constructed; it consists of a glass plate or cylinder which is made to revolve against a cushion supported on a glass pillar, but connected with the earth by a metallic chain; the electricity of the glass is excited by its friction

with the cushion, and a large metallic tube, named the Prime Conductor, being placed insulated before the plate or cylinder, receives from it the electricity evolved.

Electric excitation in different bodies or under different circumstances exhibits different phenomena, whence a distinction is established of two electric states. If a glass rod be rubbed with a woollen cloth, on approaching to it a light body, as a bit of cork, the cork is first attracted, and then repelled; but if a rod of sulphur be excited by friction with the cloth, the cork is the state in which it is repelled by the glass is attracted by the sulphur, and it is repelled by the sulphur when in that state in which it is attracted by the glass. If a pointed conductor, as a needle, be presented to the glass, a round lucid point appears on its extremity in the dark; but if presented to the sulphur, a pencil of rays seems to issue from the needle. Both are excited therefore, but still the phenomena they display are dissimilar. And if two bodies in these different electrical states be brought into contact, they attract each other; the electricity in the one appears to destroy that in the other, and the electrical phenomena cease. These two electricities being first obtained, the one from glass, the other from resinous bodies, by friction, were named the Vitreous and the Resinous, and were regarded as essentially different.

It was discovered, however, that when two electrics are rubbed against each other, the one acquires the one electricity, the other the other. Thus, in the common electrical machines, when the cushion is insulated, on friction being made it exhibits the resinous, while the glass gives the vitreous electricity. And, by employing different substances to excite friction, or by altering the surface, the same electric may be made to exhibit, either electricity, glass

the resinous, and sulphur or sealing-wax the vitreous. Franklin, from these facts, was led to explain the phenomena on a more simple hypothesis,—that there exists only one agent by which they are produced, a fluid highly elastic, or repulsive of its own particles, but attracting and attracted by the particles of other matter;—that in all bodies a portion of this principle is present, and when present, in the proportion natural to each, they exhibit no electrical phenomena; but if subjected to certain operations, as friction, the equilibrium is disturbed, and the body acquires more, or has less, than its natural proportion. In the former case it is said to be electrified *plus*, and presents the phenomena ascribed to what was called vitreous electricity: in the latter it is said to be electrified *minus*, which corresponds with the state of resinous electricity; and hence, instead of these terms, the phrases Positive and Negative electricity are employed in the Franklinian theory. This hypothesis accorded with the general phenomena of electricity, and explained very well the excitation of the different states in the common machine, where the silk cushion becomes negative, while the glass becomes positive, the former being conceived to yield a portion of its electricity to the latter. It has never however been established by any rigorous evidence, and all the phenomena may even be explained on the opposite system. The principal advantage of Franklin's system is its superior simplicity. On the other hand, the phenomena of galvanism prove that the two electricities, whatever may be their nature, exert different chemical agencies; and it is therefore more necessary, in their chemical history, to distinguish between them.

The electric states are excited by other causes than friction. The contact of some bodies, even when made with every precaution to avoid friction, alters the electric equilibrium, causing one to become positive and the other negative; or at least the bodies after their separation are found to be in these states, and such a relation exists between the assumption of these states and the chemical constitution or nature of bodies, that some are disposed to become positive, others negative. Change of temperature, too, frequently excites the different electrical states: fusion, congelation, vaporization, and the condensation of vapour have a similar effect, and it seems often to arise from chemical action. There is another singular mode in which they are assumed. If a conductor in its natural state be placed within the influence of one that is excited, but not in contact with it, placing, for example, a rod of metal insulated, at a little distance from an excited electric, the extremity of the rod directly opposed to the electric passes into the opposite state of electricity, while the other extremity passes, on the other hand, into the state the reverse of this. This is named Electricity by induction or position.

The electric states of bodies are connected with attractive and repulsive agencies, and the following general laws are established in reference to these states, with regard to these. *First*, Bodies in the same state of electricity, whether positive or negative, repel each other. The body A being positive, will repel the body B also positive; or if both are negative, they will equally repel. *Secondly*, Bodies in different states of electricity attract each other; the body A being positive, and B being negative, they will display a mutual attraction, which will cause their approximation and contact. *Thirdly*, A body in the natural state is

attracted by a body either positively or negatively electrical. *Lastly*, two bodies in different electric states, when brought into contact, neutralize each other; the electric state in each of them ceases, and their mutual attraction therefore ceases to operate. These attractions and repulsions operate at very sensible, and even if the electric excitation be high, at very considerable distances. They are concerned in the production of chemical phenomena, principally under that modification which constitutes galvanism.

Electricity is connected both with light and caloric. In its passage through certain media, it is often highly luminous, and it is capable of exciting intense heat.

Under the form of what is named the Electrical Spark, it produces an elevation of temperature sufficient to kindle inflammable bodies. And when discharged in a state of higher intensity from a coated jar, or from an entire battery, a much more intense heat is excited, so as to melt the most refractory substances. Its power of increasing temperature appears in part to depend on the resistance opposed to its conveyance through bodies. Hence, if it is not rapidly accumulated, no sensible heat is produced; as, for example, when the bulb of a thermometer is placed in an insulated metallic plate, and electricity is communicated. But, if the bulb be placed in a less perfect conducting medium, the temperature is raised. Or, if a discharge of given intensity from an electrical battery be transmitted through a metallic wire of considerable thickness, it will not produce much heat, while, if transmitted through a wire of the same metal of less diameter, an intense heat is excited.

The fusibilities of different bodies, of the different metals for example, estimated from the action of electricity on them, are different from their fusibilities, estimated from



the direct communication of caloric, no doubt from the heat excited by electricity being dependent not merely on the quantity communicated, but on this modified by their relative conducting powers, and perhaps on their elasticities, in consequence of which vibrations are more or less easily established among their particles.

Electricity, from its power of exciting heat, is applied to favour chemical combination: it affords the most convenient mode of promoting by heat the combination of elastic fluids. The apparatus employed is a strong glass tube, Pl. III. Fig. 22, closed at one end, the sides of which, at about the distance of two inches from this extremity, are perforated with small holes, in which are fixed by cement two metallic wires, the extremities of which within the tube are distant one-fourth of an inch. This instrument being filled with water or quicksilver, and inverted, the gases intended to be combined, mixed in the due proportion, are introduced, so as to depress the fluid an inch or more beneath the wires. The electric spark is made to pass from the one wire to the other, by connecting one of them with the conductor of the common electrical machine in action, and hanging a chain on the other. In the mixture of some gases, a single spark is sufficient to cause the combination to proceed through the whole mixture. In other cases, a stream of sparks requires to be transmitted to produce the combination to any perceptible extent.

By the same agency, electricity is able to effect chemical decomposition. If the spark is taken in a compound gas, it separates its constituent parts; if an interrupted electrical discharge be sent through water, it is attended with the disengagement of a small quantity of elastic fluid,

which is a mixture of the two gases which form water. Some solids are decomposed in a similar manner.

Electricity is farther connected with light. In passing from one conductor to another, it exhibits a luminous spark; when discharged through a rarified elastic medium, it presents a more diffuse and lambent light: a transparent liquid through which it is transmitted, if the quantity be not large proportioned to the discharge, is rendered luminous; or over the surface of a solid, receiving a powerful discharge, a brilliant illumination is produced. This electrical light consists of the different refrangible rays. Priestly observed these by a prism; and Morgan remarked, that they may be made to appear according to the medium in which the electric spark is taken, the light being of different colours according as a particular ray predominates.

The chemical agencies of electricity are as yet but imperfectly developed, and there are a number of facts which prove it to be absorbed or evolved in chemical changes where its influence has scarcely been traced. The electrical phenomena exhibited by the tourmalin shew that it is excited, and its different states produced, in some cases merely by variations of temperature. The experiments of Wilcke and Æpinus prove that in fusion and congelation the different electricities are excited, and the states of *plus* and *minus* produced in the body which has suffered the change of form, and the matter with which it has been in contact during the change: this happens too in the formation and condensation of vapour, and Volta traced it in different cases of chemical action. The observation of such facts becomes more important since the connection of electricity with galvanic phenomena has been established, and

that connection itself more clearly demonstrates the importance of electricity as a chemical power.

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## SECT. II.—Of Galvanism.

GALVANISM, there is every reason to believe, is the same principle as electricity. Its effects, however, its mode of production, and the laws which it observes in its action, are so far peculiar, that it is proper to consider it under a separate section. Our knowledge of this agent is of recent date. Galvani, an Italian physiologist, observed the first striking phenomenon which led to the discovery of the principle which has from him derived its name. He observed it only in its power of affecting the animal system, and it is to Volta that we are principally indebted for the theory of its production, and the development of its chemical powers. It had been discovered by Galvani, that contractions are excited in the irritable parts of animals, when a communication is established by a metallic arc between the nerve and the muscular fibre; and he concluded, that this is owing to the communication of electricity generated by the animal system. Volta supposed, that the electricity producing the contraction, and producing likewise sensations in sentient organs, is derived not from the living system, but from the action exerted between the metal and the humid animal fibre,—a conclusion which he soon demonstrated, by the discovery that it is evolved by arrangements wholly unconnected with any process of vitality. This discovery also gave a method of

augmenting the galvanic energy, enabled us to investigate its effects with more precision, and led to the discovery of its chemical agency.

The simplest voltaic arrangement is that of two different metals in contact with each other, with the interposition of a humid substance: electricity is evolved by this so as to affect sensibly sentient organs. With a repetition of the series the effect is increased, and the usual arrangement consists of a series of metallic plates arranged in a determinate order, with the interposition of certain humid conductors of electricity. The pile, the form which Volta principally employed, is constructed by commencing with a plate of silver or copper three or four inches square: on this is placed a plate of another metal, as zinc, and on this a piece of card moistened with a saline solution: this series of copper, zinc, and moistened card placed over each other, is repeated, preserving always the same order, and when 30 or 50 pieces of each have been accumulated, terminating with a plate of zinc at the top, as represented Fig. 57 Pl. III. Between each pair of plates a certain quantity of electricity is generated; in the whole arrangement, we have the accumulated action; and the effects are proportional to this. The extremities of the series are in different electrical states, that commencing with the copper being negative, that with the zinc positive: hence if a wire from each be brought in contact, electric attraction is exhibited; if the wires are applied to living matter, sensations and contractions are excited; and they also give the electric spark, and affect the electrometer. In the middle of the series the electric equilibrium exists, and hence a wire from the middle plate exhibits no electrical effect. Another arrangement similar in principle employed by

Volta, is that which he named *Couronne de Tassés*, represented Fig. 26., consisting of a series of cups, in each of which are placed a plate of zinc, and a plate of silver or copper, surrounded with a solution of salt; the plate of silver in the one cup being connected with that of zinc in the other, and the same order being preserved as in the construction of the pile.

An apparatus, the same in principle, and not very different from the latter in form, was invented by Mr Cruickshank, the Galvanic Trough as it is named, which, being possessed of every advantage, is now always used. It consists, Fig. 28. Plate III. of a hollow box or trough, of hard wood, in the sides of which are cut grooves, at the distance from each other of from  $\frac{1}{4}$  to  $\frac{1}{2}$  of an inch, according to the width of the box. Plates of two metals, generally of copper and zinc, from 3 to 6 or 8 inches square, are soldered together, and this soldered or double plate is inserted in the first groove of the box, and fixed in it by a cement of resin and wax, so well applied that no liquid can pass through. This is repeated, fixing a double plate in each groove, and taking care that the order in which they are inserted shall not be reversed, but that the copper side shall always be towards one hand, the zinc to the other. The cells or cavities between the grooves are designed to contain the fluid by which the galvanism is excited, or serve the same purpose as the moistened cards in the pile of Volta.

This form has been improved by keeping the plates detached; instead of soldering the two together: the connection between them is established at the upper edge by a metallic arc; the cells of the trough are formed by partitions of glass, or the entire trough with its partitions is made of earthen ware. The plates of copper and zinc are

introduced, so that the one shall be on one side of the partition, the other on the other, the connecting arc passing over it, and a plate of each metal being thus placed in each cell. This arrangement has the advantage, that both surfaces of each plate being acted on, a greater power is obtained, and the state of the plates is more distinctly perceived. It is represented Fig. 25.

The metals used are generally zinc and copper, and these, on the whole, answer best. The number of plates and their surface is regulated by the purpose to which the trough is to be applied. Different liquids are employed to fill the cavities of the trough, and differ much in power. With water the effect is inconsiderable; with a solution of muriate of soda, or muriate of ammonia, it is greater; it is still more so, though it ceases sooner, with muriatic or nitric acid, largely diluted, and, for different purposes, liquids of peculiar composition and strength are best adapted, as is immediately to be stated.

Though arrangements, such as have now been described, are most powerful, there are others productive of galvanism to a certain extent. The action between a single metal and a liquid gives signs of it, extremely feeble, and displayed therefore only in the most delicate test of this power,—the contractions it produces in living irritable parts, but no accumulating series of this kind can be formed. If, however, the metal be acted on at its opposite sides by two different fluids, a galvanic arrangement is formed, the power of which increases by repetition. Even charcoal, in contact with one of its surfaces with one liquid, and at another with a different liquid, forms a weak galvanic power; and one, still weaker, is formed from the contact

of different kinds of animal matter. Metallic matter, therefore, is not essential to its production.

Galvanic electricity passes through those substances which conduct electricity in its common form, though with less facility. Metals conduct it rapidly, but there are other substances which admit of the passage of electricity, which partially insulate galvanism; such is water, or dry animal membrane. But these differences arise merely from the lower state of intensity of voltaic electricity, and therefore do not appear when that intensity is sufficiently raised. Glass is a perfect non-conductor.

Its effects on living animal matter are similar to those of electricity. It excites contractions in irritable parts, and sensations in sentient organs, more or less considerable, according to its intensity. ✕

In its transition from one conductor to another, especially when the conductor is an imperfect one, it produces intense light, as, for example, in bringing into contact the wires from each extremity of the battery, or pieces of charcoal or plumbago in communication with each wire. This light appears to be the result of the accumulation of the galvanism or of the restoration of the electric equilibrium, by the contact of the two conductors in the two different states. It does not arise from any combustion, for little of the charcoal is consumed, and it can be made to appear under water and other liquids. From a battery of a great number of plates in high action, the spark can even be taken at a distance.

Galvanism is the source of intense heat. If a very fine metallic wire be stretched between metallic rods, connected with each extremity of the galvanic battery, its temperature is raised; and if the distance be not too great, to

such an extent as to melt even the most refractory of the metals. Fine metallic leaves, suspended from the one rod, are made to burn when touched with a metallic plate in communication with the other. From this arrangement, even gold and silver enter into vivid combustion; and by powerful batteries the greatest degrees of heat, capable of being produced by artificial arrangement, are obtained; the most infusible substances, the simple earths, for example, being perfectly fused.

No satisfactory explanation can be given of the heat thus evolved. It is evidently connected with the neutralization of the two opposite electricities by the contact of the positive and negative wires, and the consequent restoration of the electric equilibrium. But how this should give rise to it is not apparent. From being so intense, and capable of being indefinitely kept up while the electric action proceeds, it evidently cannot be explained on the usual principle of a change of capacity for caloric; and as it thus establishes another source of heat, the conjecture has been advanced, and must be admitted to be a possible one, that the evolution of heat in chemical combinations may not always arise, especially where it is sudden and intense, from changes of capacity, but sometimes from electrical changes connected with chemical action. Such changes being momentary, may not admit of being traced; but there are some grounds on which it may be inferred that they occur, and they may give rise to such an effect.

The most important chemical property of this power is that of producing decomposition. Very soon after the invention of the voltaic pile, it was observed by Messrs Nicholson and Carlisle, that when wires, connected with the two extremities of it, are placed in a portion of water,



a stream of gas arises from each wire, an appearance which they found owing to the decomposition of the water. The subject was immediately prosecuted, and a number of chemical compounds were found to be decomposed in a similar manner. And such is the energy of this force, that even substances most difficult of decomposition, or those least favourable to its action, such as compounds, solid and insoluble, are decomposed when a powerful battery is employed.

The decompositions produced by galvanism consist in the separation of the elements of a compound from their state of combination, by the attraction uniting them being suspended by the galvanic force: and these decompositions are attended with a singular circumstance, that the elements of the decomposed compound are not evolved together, but the one appears at the wire connected with the one extremity of the galvanic battery, and the other at the wire connected with the other extremity. To account for this, different hypotheses were proposed, not very satisfactory. At length Messrs Hisinger and Berzelius, from experiments on the decompositions of a number of neutral salts in solution placed in the galvanic circuit, drew the general conclusions, that "when electricity passes through a liquid, the principles of that liquid separate, so that some are collected around the positive pole, the others around the negative pole;" and "that the principles which collect around each pole have a certain analogy; combustible bodies, alkalies and earths pass to the negative side; oxygen, acids, and oxidated bodies pass to the positive." They farther shewed, that these forces operate at considerable distances, and that in consequence of this the transfer

of ponderable matter is effected to distant points. Grotthius had announced the same general principle. And Mr Davy afterwards confirmed it by a number of experiments, ingeniously varied, so as to shew the transfer of the elements of the compound and other facts connected with it.

Thus, employing two vessels of glass, or, as less liable to be acted on, of agate, or of gold, connected by a few fibres of the mineral substance named asbestos, moistened with water, and placing in them the solution of a compound of a salt, for example, composed of an acid and an alkali; on placing in the one a wire from the positive side, and a wire from the negative side in the other, in a short time, when a sufficient power was employed, the principles of the salt were separated, the acid collected in the one vessel, and the alkali in the other. If the solution of a salt be placed in one vessel, and distilled water in the other, either the acid, or the base of the salt, may be transferred through the communicating substance to the distilled water, according as the solution is connected with the positive or the negative side of the voltaic battery: if with the positive side, the acid remains, and the base is conveyed to the water; if with the negative side, the reverse is the result; and in this way, even metals can be transferred, as silver from nitrate of silver, or insoluble earths, as magnesia, from sulphate of magnesia. When the vessels themselves are composed of substances susceptible of decomposition, the same separation of elements is effected, though, from the state of cohesion, more slowly. Even glass is liable to this decomposition. And such is the force of this agent, that the most minute portion of a substance attracted by either of the wires is collected around it,—a circum-

stance which has frequently been the source of deception in galvanic experiments, with regard to the apparent formation of new products.

So completely is the matter conveyed by the galvanic influence protected by it, that it may be transmitted through a substance to which it has a chemical affinity, without being retained. If a strong force of cohesion, however, interfere, the substance is intercepted: thus, sulphuric acid is not transmitted through solutions of barytes, or strontites, nor these earths through sulphuric acid. The chemical affinities of the conveyed substance are suspended by the galvanic influence; an acid, for example, not reddening a vegetable colour in its progress, but only where it is collected around the positive wire; and an alkali, in like manner, exerting its chemical action only at the negative side. These decompositions, too, appear to be always complete, or the law of chemical affinity, that an ingredient of a compound, when separated from a combination, often retains a portion of the ingredient with which it had been combined, is counteracted; the transferred substance, Mr Davy found, being perfectly pure.

By all these researches, then, the general law is established, that when compounds are placed in the galvanic circuit, their elements are separated from the state of combination in which they exist, and, according to their peculiar nature, are collected,—some around the positive, others around the negative galvanic pole. How this is effected, whether by attractions alone exerted at each pole, by repulsions, or by both the element attracted to the one being repelled from the other, is not so apparent. Grotthius, in explaining the galvanic decomposition of water,

had advanced the conjecture, that as in the voltaic pile each pair of plates has its negative and positive poles, it may establish a similar polarity among the elementary particles of a portion of water interposed between its principal poles; one element may acquire the positive, the other the negative state; and if this happen, then, according to the laws of electricity, that which has become negative will be repelled from the negative and attracted to the positive pole, and that which has become positive will be repelled from the positive and attracted to the negative side. This explanation is extremely probable. With regard to the mode of conveyance, it may, as Grotthius remarked, be by a successive decomposition and recombination of the compound between the two poles; or, what is equally possible, the decomposition may be confined to the particle at each pole, and the element receiving the opposite electricity may be repelled, while the other is attracted. In atmospheric air, bodies rendered positively or negatively electrical are attracted and repelled at considerable distances. From the low state of intensity in which electricity exists in galvanic arrangements, water is a medium with regard to it nearly as atmospheric air is to electricity evolved in the common electrical apparatus, and it may therefore allow electric attractions and repulsions to operate in a similar manner.

In the production of the different effects arising from the operation of galvanism, a different law is observed with regard to each, in relation to the structure of the galvanic arrangement. By increasing the number of plates, its power is enlarged, and, by having these plates of a large size, it is likewise obvious that the quantity generated must

be greater. But the result, rather singular, has been established, that an increase in the number of plates, without a proportional increase in their extent of surface, does not equally augment all the effects from galvanism, a different law being followed in the power of elevating temperature, of exciting sensations in the organs of animals, and of producing chemical decomposition.

This is apparent from a very simple fact. If a few large metallic plates, of a large surface, as 12 or 15 square inches, or even a larger size, two or three feet, be employed as a galvanic battery, it will be powerful in producing light and heat, and will therefore illuminate charcoal vividly, or cause metallic leaves, placed in the circuit, to burn with the utmost brilliancy. But it will display little power of electrical attraction and repulsion, will have comparatively little effect on sentient organs, and will act feebly on imperfect conductors in producing decomposition. If the same plates be cut down, each being divided into four, and a battery be constructed with these, though there is, on the whole, the same quantity of surface, yet the relation of this to repetition or number being changed, the effects are different; it has little power in burning the metallic leaves; while it exhibits more evidently the different electrical states; it excites more forcibly sensations or contractions in animal organs, and is much more powerful in giving rise to chemical decomposition.

This has been in particular investigated by Ritter, and he, from a very extensive series of experiments, has endeavoured to establish the relation between number and surface in the metallic plates in a galvanic battery, adapted to the production of each of the effects obtained from galvanism. That of exciting sensations and contractions

in animals, he found to be principally dependent on number; that of producing combustion is principally dependent on extent of surface; that of producing chemical decomposition is, in its relation to surface and number, intermediate between these. But with regard to all of them, a certain relation exists, or a certain proportion between number and surface gives the maximum, and, increasing either indefinitely, according to Ritter, diminishes the power. If the due proportion be observed, the galvanic energy displayed in all these effects may probably be indefinitely increased.

The theory of these differences probably is, that a peculiar state of intensity of galvanism is required for the production of each of these effects. The quantity of electricity generated in the apparatus will be proportional to the surface acted on, but its state of intensity is produced by its accumulation, and will therefore be regulated by the quantity of imperfect conducting, compared with perfect conducting matter in the arrangement. The liquid interposed between the metallic plates is the least perfect conducting matter: the repetition, therefore, of the metallic plates, the absolute surface remaining the same, forms an arrangement in which the imperfect conducting matter is most abundant, in which there is the greatest resistance to the evolution of the electric force, and in which therefore it will acquire the highest state of intensity. Now, a considerable intensity is requisite to enable the electricity to penetrate the animal membrane, which it must do to excite sensations or contractions, this membrane being an imperfect conductor: at a lower intensity, it will penetrate liquids, and act in decomposing them, observing a certain ratio with regard to this, according to the conducting

power of the liquid; the less perfect the conducting property is, the effect in producing decomposition being more dependent on number. And metals are conductors so perfect, that in the lowest state of intensity it will penetrate them: the repetition therefore in the galvanic apparatus is less requisite; and the effects will be in a great measure proportional to the quantity generated. Hence the cause of the peculiar relations of number and surface to these different effects: the extent of surface giving quantity, and the repetition of surface in the series or number increasing the intensity of power.

In conformity to the difference of power thus required to produce these different effects, it has been found that different liquids are best adapted to each. To excite that effect by which intense heat and light are excited, measured by the length of metallic wire which is melted, nitric acid, diluted with from 30 to 40 parts of water, is most powerful; sulphuric acid diluted is inferior in power; it adds, however, to the power of nitric acid, and the mixture is more economical than the latter alone. For producing chemical decomposition, muriatic acid is better adapted, and it has the farther advantage of its power continuing longer; eight ounces may be added to a gallon of water, or a smaller quantity to a solution of sea-salt. A solution of a neutral salt is nearly equally active with a diluted acid in producing the power which gives the shock, but is much inferior in producing the other effects.

A singular arrangement has been constructed by De Luc, in which there appears to be a separation of the electrical and chemical powers; at least, while the former are considerable, the latter are not sensibly exerted. It consists of discs of zinc and fine tin leaf, with paper interposed be-

tween each pair of metals. This very sensibly affects the electrometer, charges a jar so as to give a shock, and when the number is considerable, exhibits a spark. But it produces no chemical effect whatever. Electricity, therefore, seems to be generated in it in small quantity, but is brought to a high state of intensity.

It remains to consider the theory of Galvanism. What is its nature? And how is it produced by galvanic arrangements?

There can remain little, if any doubt, that Galvanism is Electricity. Not only are they similar in their general properties, and in the laws they observe, but their identity has been more strictly established. If two metallic plates be applied to each other, an arrangement which we know to be productive of galvanism, they are found to pass into different electrical states, the one becoming positive, and the other negative. The two extremities of a galvanic battery are likewise in these opposite states, that connected with the more oxidable metal, the zinc, in the common arrangement being positive, and that with the other metal negative. Hence wires connected with these extremities affect the electrometer, especially when a battery of a large number of plates is employed, even though their size be small. These states can even be communicated to other bodies; a weak electrical charge being given to a coated jar, and even to an entire battery, by communication with a galvanic trough, the charge being communicated with great velocity, and very nearly to the same intensity as that of the electrical force in the trough itself. And the electricity thus communicated gives precisely the same sensation or shock as electricity in its usual form: all the other electrical phenomena too, such as the passage from one



conductor to another at a sensible distance, the discharge through an imperfect vacuum, and the attractions and repulsions of light bodies, have been obtained from the action of a very powerful galvanic arrangement.

The differences which have been observed between electricity and galvanism are principally that the galvanic influence does not so easily penetrate imperfect conductors as the cuticle, charcoal, water and other liquids, and that its chemical action is more energetic, compared with its electrical energy, than in electricity evolved by friction. The cause of these differences appears to be, that galvanism, considering it as electricity, is in a low state of tension. That it should be in this state, appears to follow from the nature of the arrangement by which it is generated, which, consisting of a series of conductors, it is little accumulated, but is carried off as rapidly as it is produced, while, from the nature of the electrical apparatus, which consists of less perfect conducting matter, this does not happen; it is evolved less rapidly, and accumulates to a higher state of intensity. That galvanism does exist in this state of low intensity, appears from the spark from a galvanic battery being so small, and unable to overcome the resistance of the air; if the points of the conducting wires be at a very small distance. And its rapid evolution in this state appears from this, that a charge of low intensity can be communicated from the pile to a series of coated jars of extensive surface by a single contact, while to give a similar charge from a very powerful electrical machine would require repeated contacts. It is farther found, that when arrangements are formed, which produce a stream of electricity in constant evolution, its effects are similar to those of galvanism; Wollaston, by whom the experiment was first

made, having shewn, that from very fine silver wires coated with wax, and connected with an electrical machine in action, effects were obtained in decomposing chemical compounds similar to those which would have been obtained from connection with a galvanic battery; and Davy, employing a similar arrangement, found that the principles of the decomposed substance are conveyed to a distance, and collected around the positive and negative wires, as they are by galvanism in its usual form.

On the principle that electricity and galvanism are the same, it remains to be determined by what cause it is evolved, and put in motion in the galvanic arrangements. Two explanations have been given of this subject, one proposed by Volta, the other originating in the researches of Fabroni and of some British chemists.

Volta's hypothesis rests on the following fact, that "if two different metals, perfectly dry, insulated, and having only their natural quantity of electricity, be brought into contact, on removing them from that contact, they are in different electrical states; the one is positive, the other negative." In the example of the metals generally used in galvanic arrangements, the zinc will be found in the former state or *plus*, the copper in the latter or *minus*. The difference is not very considerable; it is perceptible, however, and, when accumulated in an electric condenser by repeated application of the plates, becomes sufficiently strong to cause the electrometer to diverge. Electricity, therefore, is developed by the contact of different metals, independent of any foreign action on them; or one metal, by its contact with another, forces part of its electricity into that other, and this inequality of distribution continues while they are in contact, and no conductor is applied to

them. On this principle the excitation of electricity by galvanic arrangements is explained in the following manner.

If a series of metallic plates were constructed, without any intermediate substance, no accumulation of power would be obtained. The copper, for example, commencing this series, and in contact with a plate of zinc above it, would yield to it part of its electricity, and the zinc would become positively charged. But if another plate of copper were placed above the zinc, this action would be interrupted; the zinc being in contact at each of its surfaces with the two plates of copper, two equal forces would act in opposite directions, and destroy or counterbalance each other. The difference in the electrical state, therefore, of a series thus formed, would not be greater in the whole, than in a single pair of the plates, and would even amount to nothing if the arrangement began and ended with the same metal. But if a piece of moist card or cloth be placed between the plates, that is, between the zinc plate and the second copper plate, the effect of the latter on the former is interrupted: the liquid in the card having comparatively with the metal little of this peculiar electro-motive power, or property of breaking by contact the equilibrium of electricity, does not check the action, but acting as a conductor, conveys the positive electricity from the zinc to the next copper plate; and accordingly, on this addition of the moistened card, Volta finds, by experiment, that signs of electricity are manifested. By continuing the series the power is always increasing, the action is renewed at each pair of plates, the electricity communicated is always given at the expence of the pieces beneath; these therefore become negatively charged in a progressive or-

der downwards; the others become positively charged in a similar order upwards: the two plates in the middle of the column are in the natural state; and as highly negative as the copper commencing the series is, as highly positive is the zinc plate which terminates it, the difference being greater according to the number of plates. The different powers of the different metals in affording galvanism, Volta ascribes to the different degrees in which they possess this electro-moving power, or to the effect of breaking the electric equilibrium, being greater in some than in others, zinc taking electricity from every other, and gold yielding it to the rest. The powers of different liquids in exciting galvanism, he supposes owing to their greater conducting power, modified as they have less of the electro-motive quality; and he shews by experiment, that saline liquors, which are superior to water in exciting galvanism, are superior in conducting power. The action which puts the electrical energy in motion, though greatest between the metals, is not peculiar to them; it exists, though to a less degree, in other substances, and hence a galvanic series can be constructed without metallic matter. And were we possessed of any solid substance capable of conducting electricity without having the electro-motive property, we might by means of it construct a galvanic battery without the intervention of any liquid.

The hypothesis opposed to this, considers the excitation of galvanism as the result, not of the electrical action of the metals on each other, but of the chemical action of the liquids employed in the construction of the galvanic series on the metals composing it. It is conceived, that in consequence of this action the metal suffers a change in its relation to electricity; whence electricity is evolved at the

surface, which is acted on. This determines the motion of the electrical power to that surface from the rest of the mass of metal. Hence, supposing a plate of zinc to consist of a number of layers, the external layer acted on by the liquid giving out its electricity, and the other layers yielding a corresponding portion in their turn, the electricity in the entire plate is put in motion, and the direction is from the opposite side of the plate towards that which is suffering the chemical change. The latter becomes positive, the former negative; and this last state is of course communicated to the copper plate which is in contact with that surface of the zinc. Were the next plate in the series to be zinc, the same chemical action would be exerted by the liquid at its surface. The same evolution of electricity would in consequence be produced, and this would be in a direction contrary to that from the other. But the next metallic surface being copper, and this metal not being much acted on by the liquid, this is prevented; the copper receives, by the medium of the interposed liquid, the electrical state of the preceding pair of plates, which it communicates to the zinc connected with it. At the surface of this zinc plate exposed to the action of the liquid, the same action goes on as in the former: a fresh portion of electricity is evolved in consequence of it, and this must be supplied from the plates behind; this is repeated at each pair of plates in the series: the copper plate therefore at the commencement is becoming more highly negative, and the zinc plate which terminates it is proportionally positive. Thus, according to this hypothesis, the evolution of electricity depends entirely on the chemical action of the liquid on the metal which is most susceptible of that action, and the other metal is useful only in that it is

not chemically acted on to any great extent, and does not therefore, by any contrary evolution of electricity, counteract the effect produced at the surface of the metal suffering the chemical change.

This last hypothesis appears to be in a great measure gratuitous, while Volta's explanation has the important advantage of resting on a fact which is apparently sufficiently established, that two metals, by mere contact, alter the electric equilibrium, and pass into the different states, and this independent of any chemical action or change. The fact appears also to be proved, that saline liquids are better conductors of electricity than water, while they have little of this electro-motive power. Hence it appears to follow, that from such an arrangement as that which constitutes the voltaic apparatus, a stream of electricity must be put in motion, and the two extremities of the series must be in the opposite electric state.

There are some objections, however, to this explanation, and some facts in favour of the opposite opinion, that the evolution of galvanism is in part at least owing to chemical action. The power of the metals seems to be in some measure connected with their susceptibility of being chemically acted on; zinc, for example, which is the most oxidizable of the metals, forming the most powerful arrangement; and even in the subversion of the electric equilibrium, by the mere contact of the metals, there appears to be some connection between the electro-motive equality, and their chemical agencies, that metal of the two always becoming positive which has the strongest attraction to oxygen. The power too of the interposed liquids, in exciting galvanism, does not appear to be proportional merely to their superior conducting power, but to be connected with the che-

mical action they exert; those being most powerful in exciting it which act chemically with greatest energy, and the excitation in a great measure ceasing when that action is suspended. Yet the opposite fact appears also to be established, that the power of certain liquids in exciting galvanism is more than proportional to their chemical action; alkaline solutions, for example, or solutions of sea-salt or sal-ammoniac, affording next to diluted acids, the liquids best adapted to excite galvanic action, though they do not exert any great chemical energy; and in comparing them with these acids, their exciting power is unquestionably much greater than their chemical action. If chemical changes, therefore, operate in the production of galvanic electricity, it is probably only as a subordinate cause, modifying the more important one from the electro-motive power: and the principal obscurity still remaining in the theory, is with regard to the mode in which these changes have this modifying effect. Of this no very satisfactory explanation has been given.

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## PART II

### OF THE CHEMICAL PROPERTIES AND COMBINATIONS OF INDIVIDUAL SUBSTANCES.

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**T**HE Science of Chemistry divides itself into two great departments,—the one including its general principles, or the statement of the phenomena and laws of those forces from the operation of which chemical changes arise; the other comprising what relates to the operation of these forces on individual substances, embracing therefore the history of the combinations of matter, and the chemical agencies of all known bodies.

I have given the outline of the methods, according to which substances may be classed, in conformity to their chemical relations. The table of the arrangement I have framed is prefixed to the first part of this volume, and it is unnecessary to repeat the observations with which it is accompanied. The first place is given to Atmospheric Air and its Elements, as there are no substances, the chemical actions of which are more important and extensive, and none therefore with which it is more necessary to be acquainted, in proceeding to the details of the science.



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**BOOK I.****OF ATMOSPHERIC AIR AND ITS ELEMENTS.**

**T**HE atmosphere is that mass of elastic fluid which surrounds the globe. This air was regarded as an element in the system of ancient philosophy; and one of the most brilliant results of modern chemistry is the discovery of its composition, which we owe to Scheele. It consists of two æriform bodies, oxygen gas, and nitrogen gas; with which are mixed, a small portion of another elastic fluid, carbonic acid, probably originating from accidental sources; and watery vapour, derived from the evaporation of water at the surface of the earth. The two latter are therefore scarcely regarded as essential to its constitution.

The composition of atmospheric air is demonstrated both by analysis and synthesis. The analysis is performed by submitting it to the action of substances which combine easily with oxygen gas, and reduce it from the ærial form, such as phosphorus, or the compound of sulphur and lime dissolved in water: a diminution of volume, amounting to about a fifth part, is produced from the abstraction of oxygen; the residual air is nitrogen. The synthetic experiment consists in mixing oxygen and nitrogen gases in the due proportions; an elastic fluid is formed the same as atmospheric air. To be enabled to explain the chemical agencies of the compound, it is necessary first to describe the properties of its constituent elements.

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## CHAP. I.

### OF OXYGEN GAS.

**T**HIS elastic fluid was discovered nearly about the same time by Scheele and Priestley. It received the appellations of Fire Air, Dephlogisticated Air, Pure Air, and Vital Air, terms superseded by the name of Oxygen, derived from a chemical property eminently characteristic of it, that of giving sourness or acidity to the compounds in which it predominates. Oxygen denotes its gravitating matter or base; Oxygen Gas is the name given to it in its elastic form.

This aëriform fluid is extensively diffused. It not only exists as a constituent part of the atmosphere, but it is also the principal component part of water; it exists in all acids, in the alkalies and earths, and is found in numerous forms of combination in mineral substances, and in the products of the vegetable and animal systems.

It is from some of its compounds that it is obtained insulated. That which affords it most readily is the mineral substance known by the name of Black Manganese. This consists of a peculiar metal, manganese, united with oxygen. If exposed to a full red heat, a large portion of the oxygen is expelled in the aërial form; the elevated temperature weakening its affinity to the metal, and allowing it to escape from the combination, until the increase thus produced in the relative quantity of the manganese to the oxygen that remains, adds so much to the force of its at-

traction, that the farther decomposition is prevented, a portion therefore still remaining combined with the metal. The expulsion of the oxygen from the black oxide of manganese is much facilitated by the introduction of another affinity; hence if mixed with its own weight of sulphuric acid, a large quantity of oxygen gas is disengaged from the mixture by the moderate heat of a lamp; the acid favouring its escape, by the attraction which it exerts to the manganese, in a low state of oxidation. Other metallic oxides, as the red oxide of mercury, or the red oxide of lead, afford a portion of oxygen by similar processes; a large quantity, but less pure, is obtained when nitre is decomposed by heat in an earthen retort: another salt, the oxymuriate of potash, affords it, when exposed to a red heat, and in a state more pure than that in which it is obtained by other methods.

Oxygen gas is colourless, and destitute of smell or taste; it is rather heavier than atmospheric air; being about 1103, the latter being 1000. 100 cubic inches weigh 34 grains.

It is absorbed by water, but in very sparing quantity; 100 cubic inches of water, freed from air by boiling, absorbing about 3.5 cubic inches, under a common atmospheric pressure, and at the temperature of 60°. By increasing pressure, a larger quantity is absorbed, proportional to the pressure applied; and, under a great pressure, water may be made to take up about half its bulk of the gas, acquiring, however, from this impregnation, no taste or smell.

The most characteristic property of oxygen gas is its power of exciting and supporting combustion. An inflammable body kindled, on being introduced into it,

burns with increased brilliancy; it also burns longer, and is more quickly consumed, and much more heat and light are evolved, than when it burns in atmospheric air; even bodies which do not suffer combustion, when raised to a red heat in atmospheric air, as iron, burn rapidly when they are at this temperature immersed in oxygen gas. Strictly speaking, it is the only gas that supports combustion, atmospheric air and others doing so only from the oxygen they contain. During the burning, the oxygen is consumed; and hence a given quantity of it can support the process only for a limited time. The product of the combustion is frequently a substance having acid properties; and from this oxygen has been regarded as the principle of acidity.

Oxygen gas is equally powerful in sustaining animal life by respiration. If an animal be confined in a given quantity of it, it lives a longer time than it would do in the same volume of atmospheric air. A quantity disappears, or is consumed during respiration, and is indispensable to the continuance of life; and atmospheric air, or any gas, sustains life, only from the oxygen it contains and is capable of affording to the blood. Pure oxygen gas, however, is not well adapted to animal existence. If an animal be confined in a given quantity of it, its respiration becomes hurried and laborious before the whole of the oxygen is consumed, and it dies even though oxygen is still present in quantity sufficient to support life for some time in another animal of the same species. Hence the adaptation to animal life of an atmosphere such as ours is, in which oxygen is in a more dilute state.

The peculiarity of oxygen deserves to be remarked as intimately connected with its chemical agencies, that of all

bodies it appears to have, in the highest degree, that relation to electricity, in consequence of which it is attracted, when under electrical influence, to the positive electrical pole; it even impresses this property on the compounds in which it predominates, and they alone possess it.

Oxygen has a tendency to combination, more extensive perhaps than any other simple body: all the products of combustion are compounds of it, and are numerous and important agents in chemistry. The acids are of this kind, and their activity is principally dependent on the oxygen they contain. All the metals are capable of combining with this principle. And it exists in an immense number of natural substances. Its affinities are also more numerous and more energetic; the development of its agencies formed the principal part of what has been named the modern theory of chemistry, and they still afford the most important relations of the science.

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## CHAP. II.

### OF NITROGEN GAS.

**T**HIS elastic fluid remains after the removal of oxygen from atmospheric air, by the processes which have been described. It is most easily procured by burning phosphorus in atmospheric air, or exposing this air to the liquor, formed by boiling sulphur and lime with water: in either case the oxygen gas is abstracted, and the residual nitrogen gas is agitated with water to render it pure. It has been known by various appellations, as Corrupted Air, Mephitic Air, Phlogisticated Air. It received the name of Azote or Azotic Gas, from being, in opposition to oxygen, incapable of sustaining animal life by respiration. The more correct denomination of Nitrogen is given to it, from being the base of an order of compounds which have been long known by the name of Nitrous.

Nitrogen gas is invisible, insipid, and inodorous. It is lighter than atmospheric air, its specific gravity being to that of the latter as 969 to 1000.

This gas, possessing no very striking property, is principally characterized by certain negative qualities in its pure form, and by the nature of the compounds it forms. Thus it is incapable of supporting combustion. It is equally incapable of supporting animal life by respiration. It is not inflammable; for although it combines with oxygen, a process generally attended with the phenomena of com-

bustion, nitrogen presents the anomaly of exhibiting none of the appearances of burning during this combination; it neither sensibly evolves heat nor light. Lastly, nitrogen gas is not perceptibly absorbed by water; it suffers no apparent diminution of volume when exposed to it. If, however, the water has been previously freed from all air by boiling, and the nitrogen gas be exposed to it for some hours, a very small quantity, 1.47 cubic inch, is absorbed by 100 cubic inches of the water.

The peculiar characters of nitrogen as a substance distinct from others are better shewn in its chemical combinations. It unites with oxygen in different proportions, and forms compounds possessed of very peculiar chemical properties. It unites too with hydrogen, forming one of the alkalis, Ammonia. And it is a chief ingredient in the products of the animal system, and appears to give their most distinguishing chemical characters.

Opinions have often varied with regard to the nature of nitrogen. Priestley stated many experiments in which it appeared to be procured from water by peculiar processes, such as distilling the water from an earthen retort, or passing it through an earthen tube at a red heat. In the freezing of water, a portion of elastic fluid is disengaged, which he found also to be nitrogen; and the production of this appeared to him to be unlimited as long as the freezing was repeated, even though the precaution was taken of not admitting the atmospheric air. Girtanner, from an extensive series of experiments, affording similar results with regard to the production of nitrogen in converting water into vapour, concluded, that nitrogen is, like water, a compound of oxygen and hydrogen, containing a smaller proportion of oxygen than water does; at-

mospheric air, therefore, he supposed to be a compound of oxygen and hydrogen; and the nitrogen gas obtained from it by the usual methods he supposed to be formed by a portion of the oxygen being abstracted, and the remaining quantity combining with the hydrogen. Priestley had drawn different conclusions. Water he regarded as a simple body, and the basis of all elastic fluids, appearing under the form of nitrogen, hydrogen and others, by modifications produced on it by the operation of more subtle principles which are not capable of being ascertained by weight.

These hypotheses have been regarded as extravagant, and nitrogen gas continued to be ranked as a simple substance. Mr Davy afterwards drew some conclusions of a similar kind, from some experiments on the action of potassium on ammonia, in which there appeared to be a loss of nitrogen, and an apparent production of oxygen and hydrogen, and from others in which there appeared to be a production of nitrogen. It has since appeared that these results were incorrect: the accuracy or conclusiveness of Priestley's and Girtanner's experiments is doubtful, and the simple nature of nitrogen still appears sufficiently established. Berzelius has lately inferred, from speculations connected with the doctrine of definite proportions, that it is a compound of oxygen with an unknown base, and has even fixed the proportions of these at 44.32 of base, and 55.68 of oxygen; others have affirmed, as a consequence of this doctrine, that nitrogen can contain no oxygen,—a proof of the little value to be attached to such speculations.



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### CHAP. III.

#### OF ATMOSPHERIC AIR.

FOR the discovery of the composition of atmospheric air, chemistry is indebted to Scheele. The following is the experiment from which he inferred it: Having put into a bottle, capable of containing 24 ounce measures, four ounces of a liquor prepared by boiling a solution of potash on sulphur, and having closed the bottle accurately, and inverted it in water, he allowed it to remain in this situation for two weeks. At the end of that time, he opened the bottle under water, when a portion of water immediately rushed in, shewing that part of the air included with the liquor had been absorbed, or had lost its elastic form: the quantity which had disappeared amounted to six parts nearly of the original twenty. The remaining air was changed in its qualities, was lighter than atmospheric air, and incapable of supporting combustion.

Scheele had previously discovered the existence and properties of oxygen gas, and by this discovery he was enabled to explain the nature of the changes which the air had undergone in this experiment. Since it was diminished in volume, it was obvious that a portion of elastic fluid had been abstracted from it; if this had been merely a portion of the air itself, the remaining air might have been expected to have retained its properties, but since it was also changed in its qualities, and in particular was no longer capable of supporting combustion, it was evident, that it

had lost a principle which gave it that property. Scheele accordingly concluded, that oxygen gas had been abstracted from it, and that the atmospheric air is a compound of this with the residual gas, which is nitrogen. He found, what was conformable to this, that oxygen gas is absorbed by the solution of sulphur and potash, by which the diminution in the volume of atmospheric air had been produced. And he farther confirmed his conclusions synthetically, by adding oxygen gas to the residual nitrogen: an air similar to atmospheric air was produced. He found, too, that similar changes are produced in atmospheric air by other substances which are capable of abstracting its oxygen.

Lavoisier soon after advanced the same opinion with regard to the composition of atmospheric air, from experiments in which its oxygen was abstracted by burning inflammable bodies, or calcining metals, in it. From some of the compounds formed in these processes, particularly in the calcination of quicksilver, he obtained the oxygen which had disappeared, and adding it to the residual nitrogen gas, reproduced atmospheric air. He thus demonstrated its composition, both by analysis and synthesis.

The process by which the proportion of oxygen in atmospheric air is determined, has been named Eudiometry, from an opinion which at one time was entertained, that the salubrious power of the air, with regard to animal life, depends on oxygen, and that therefore by this process we might be able to ascertain this,—an opinion for which there is no foundation. Different eudiometrical methods are employed, such as the action of the liquor prepared from sulphur and potash, or sulphur and lime boiled in wa-

ter, the slow combustion of phosphorus, the detonation of the air with hydrogen gas, and the action of nitric oxide gas,—applications to be noticed under the history of these substances.

The proportions of oxygen and nitrogen in the atmosphere have been variously estimated, from the diversities arising from different eudiometrical processes. The proportion of oxygen has thus been stated so high as 0.25 or 0.27. The average results from those experiments that can be regarded as most accurate, are as nearly as can be estimated, 21 of oxygen gas to 79 of nitrogen gas by measure, or 23 to 77 by weight.

It has been supposed, that the composition of atmospheric air varies at different parts of the earth's surface, and also at different heights. The reverse of this, however, has been established; and by more recent experiments, made with every precaution, it has been shewn, that air, in the upper regions of the atmosphere, is the same in composition with air at the level of the sea, and that there is an equal uniformity in composition in the air of distant countries. It is also uniform, according to De Marti's experiments, in every state of the atmosphere with regard to temperature, pressure, humidity, the season of the year, or the hour of the day or night. What appears more singular, the same experiments prove, what Priestley had indeed before established, that the air of places the most offensive and unhealthy, is apparently of the same chemical composition as that of situations the most salubrious; the air of crowded cities, or of manufactories, being not less pure than that of the country: the deleterious agency, therefore, of such air, depends not on any difference in composition,

but on the presence probably of more subtle effluvia, unfavourable to health.

In the composition of atmospheric air, there remains a striking singularity to be pointed out. Its constituent gases are of different specific gravities, and therefore, were they not retained in union by a mutual attraction, it might be concluded that they must separate; the heavier, that is, the oxygen, collecting towards the surface of the earth, the lighter receding from it, and occupying the upper region,—a separation which, it appears from the preceding facts, does not take place. Yet, although they remain united, there are none of the usual indications of chemical union, no modification of properties, and even no change of density. What, then, is the nature of that constitution by which they are preserved in a state of equal and uniform diffusion?

To solve this problem, a very ingenious hypothesis has been advanced by Mr Dalton, founded on the assumption, that the particles of mixed gases neither attract nor repel, but are perfectly indifferent with regard to each other. Did they attract, Mr Dalton conceives, they must enter into intimate combination, which would be marked by a change of properties. Did they repel each other, they must separate, and be arranged according to their specific gravities. Either supposition, therefore, he concludes, is excluded by the known constitution of the atmosphere; and there remains only the hypothesis, that the particles of the elastic fluids composing it neither attract nor repel, nor are indeed at all affected by their proximity. On this hypothesis, each gas diffuses itself from the repulsion between its own particles, and there rest, upon the surface of the earth, so many columns, as it were, of these gases,

each supporting itself by its own elasticity, intimately blended with the others, but altogether independent of each other. And as the diffusion is complete, we discover, in any given portion of the mass, these gases in the same relative proportion. The same hypothesis Mr Dalton applies to the constitution of all mixed gases, the particles of which do not appear to be intimately combined.

Mr Dalton's reasoning is highly ingenious, and apparently strict. Yet a different hypothesis may also be proposed, resting perhaps on a principle more probable *a priori*, and equally adapted to explain the constitution of atmospheric air. The most correct views of chemical affinity lead to the principle, that all bodies have mutual attractions, and that these are prevented from operating, so as to establish intimate combination only by the exertion of external forces. In the action of a liquid on a solid, cohesion operates, counteracting the mutual attraction, and, if sufficiently powerful, preventing solution. In the action of an aërial substance on a solid, the cohesion of the one, and the elasticity of the other, are the obstacles to the effective exertion of the attraction exerted between them. And in the case of two aëriiform fluids, the same elasticity in each is the cause counteracting that affinity which would unite their particles. But in all these cases, it is not to be supposed that the affinity is not exerted: it no doubt operates with a certain force, the circumstances which act against it only being so powerful as to prevent intimate combination. The particles of oxygen and nitrogen gases are capable, under certain circumstances, of exerting a strong mutual attraction. Under the circumstances in which they are presented to each other in the atmosphere, this is not exerted so as to overcome the elasticity of each,

and establish that intimate combination into which, by other arrangements, they may be made to enter. But still it exists, and may so far operate as to counteract the slight difference in their specific gravity, and retain them in union. This accounts for the phenomena, and, in particular, reconciles the two facts, which appear incompatible, the uniformity of the composition of atmospheric air, while it has no properties different from those of its constituent parts. The principle, too, in the abstract, is more probable than that of the opposite hypothesis. The particles of any individual gas repel each other: why therefore should the particles of mixed gases not exert a similar repulsion? It is scarcely possible to conceive any cause for this, but the exertion of a mutual attraction not sufficiently powerful to overcome their elasticity, and bring them into intimate combination, but exerted at least with such force, as to counteract their repulsion, so as to prevent their separation. Mr Dalton's view of the subject, independent of any improbability that may be supposed attached to its principle, is farther liable to the important difficulty, that if no repulsion exists between the particles of two mixed gases, they must, in the movements impressed on elastic fluids, occasionally come into the closest contact, and it is impossible to assign any cause why they should not then enter into intimate union.

Besides the oxygen and nitrogen which principally compose the air of the atmosphere, there always exists in it a sensible quantity of a compound elastic fluid, Carbonic Acid Gas. This is easily discovered, by exposing to the atmosphere, substances which have an attraction to this gas, as lime water, or an alkaline solution; they are soon found to have imbibed a portion of it. The proportion of

this gas to the other gases composing the atmosphere is so small, that it is not easy to estimate it with accuracy. Mr Dalton has inferred, from experiment, that it does not exceed a thousandth by weight. As this gas is produced in respiration, and in other processes at the surface of the earth, the portion of it contained in the atmosphere has been supposed to be derived from these sources. This is not improbable; at the same time, from the reciprocal attraction which gases exert, it is uniformly diffused; and it appears also to be present always in nearly the same proportion, and at the greatest heights at which the air has been examined.

Aqueous vapour is another constituent part of the atmosphere; obviously derived from the evaporation of water at the surface,—an operation dependent on temperature and other causes, and therefore the proportion is not uniform. The temperature is the great cause by which the quantity is varied, and hence the proportion is much dependent on climate and season. In the torrid zone, Mr Dalton remarks, the quantity is such as to exert a pressure on the surface of the earth equal to from 0.6 to an inch of mercury: in our climate it is seldom equal to a pressure of 0.6, and in winter is sometimes so low as 0.1. The maximum or largest quantity which can exist in the air without condensation seems to amount to about 10 grains in a cubic foot at the temperature of 60, and 4.5 at the temperature of 43. The quantity increases at a high ratio as the temperature is raised. While the vapour preserves completely the elastic form, the air through which it is diffused is transparent. When condensing, it communicates a degree of opacity, and, according to the rapidity of the con-

densation, gives rise to the appearances of clouds, dew, mist, and rain.

A subject of chemical inquiry is, by what operation is water elevated in vapour in the atmosphere? and farther, what is strictly connected with this, in what state does the aqueous vapour exist? Water; being capable of passing into vapour from the action of heat alone, it has been supposed that its elevation in the atmosphere is entirely the result of temperature; the vapour formed existing, according to one view, in a state merely of mechanical diffusion, independent of any action of the permanent gases upon it, or, according to a different hypothesis, being combined with these gases by a weak attraction. According to a different theory, the transition into vapour is owing to the chemical affinity exerted to water by atmospheric air, and of course it is retained by that air in a state of solution or weak combination.

This last theory, proposed by Halley, and afterwards illustrated by Le Roy, Hamilton and Franklin, is probably the just one. A mutual affinity exists between water and the gases composing the atmosphere, for it absorbs them in sensible quantity; the same affinity must operate in enabling these gases to dissolve a portion of water, and this is promoted, like all similar combinations, by a high temperature, by agitation, and of course also by the dryness of the atmosphere. The opposite views rest on the assumption extremely doubtful, that water, independent of any chemical action of the air upon it, can pass into vapour at natural temperatures. The proof which has been usually given of this is, that water, placed *in vacuo*, passes into vapour at such temperatures. But the proof is inconclusive, for in the manner in which the experiment has been



performed by introducing water into the vacuum of the air pump, or the more perfect Torricellian vacuum; while the chemical agency of the air is withdrawn, its pressure is also removed; and although a portion of water may, under these circumstances, pass into vapour, this is no proof that the same thing will happen under the usual atmospheric pressure. The experiment to be conclusive must be performed under a pressure equivalent to that of the atmosphere, that is, equal to a column of mercury  $29\frac{1}{2}$  inches in height. But the result is then subversive of the hypothesis; for water, under that pressure *in vacuo*, does not sensibly evaporate.

It is probable, therefore, that the spontaneous evaporation of water, exposed to the atmosphere, depends principally on the attraction exerted to it by the elastic fluids which form atmospheric air, and the aqueous vapour may be regarded as in the same state of slight union with the other gases composing it, as they are with each other. The only difference is, that they being so far distant from the point at which they assume the aëriform state, are not affected by natural changes of temperature, while these changes must affect the combination so far as it relates to the aqueous vapour.

Another chemical question of considerable interest, but still involved in difficulty, relates to the causes by which water is precipitated from the atmosphere. It is obvious, that it may be occasioned by reduction of temperature, but it is not easy always to trace this cause, and especially to account for that sudden and copious deposition which constitutes rain. Hutton advanced the hypothesis, that the solvent power of air, with regard to water, is increased by temperature in a higher ratio than the increase of tempe-

perature itself; this appears to be confirmed by subsequent experiments. The consequence of it is, that if two portions of air, at different temperatures, are mingled, as they may be in the atmosphere by winds, the whole quantity, if each has been previously saturated with humidity, will be incapable of retaining in solution all the water which the separate portions held dissolved: a quantity therefore will be rapidly separated, and its particles, uniting and meeting with resistance in their descent, will coalesce so as to form rain. Electricity has sometimes been supposed to be concerned both in the spontaneous evaporation of water, and in its deposition from the atmosphere; but the facts with regard to this are not well ascertained, nor is the agency of this cause well understood.

The atmosphere, then, so far as its constituent parts can be ascertained by chemical analysis, consists of oxygen, nitrogen, carbonic acid, and aqueous vapour; the three first are in constant, the last in variable proportion; but taking the mean, the following may be given as the relative quantities of these principles.

|                    |      |             |       |            |
|--------------------|------|-------------|-------|------------|
| Nitrogen gas,      | 77.5 | by measure, | 75.55 | by weight. |
| Oxygen gas,        | 21.  | _____       | 23.32 | _____      |
| Aqueous vapour,    | 1.42 | _____       | 1.03  | _____      |
| Carbonic acid gas, | .08  | _____       | .10   | _____      |

The properties of atmospheric air are merely those of its constituent gases, weakened by their mutual dilution. It is invisible, insipid, inodorous, compressible, and permanently elastic. Its specific gravity is .0012279,—the medium, as nearly as can be estimated, between the specific gravities of oxygen and nitrogen gases, in the proportions

in which they are mixed in the atmosphere. 100 cubic inches weigh 31 or 30.5 grains.

Atmospheric air supports combustion, a power dependent on its oxygen. From the operation of the same principle, it sustains animal life in respiration. The action of the nitrogen is negative in both processes; it serves therefore merely to weaken the action of the oxygen.

Water absorbs atmospheric air, though in sparing quantity. The absorption, too, is unequal with regard to its constituent parts, more of the oxygen being absorbed than of the nitrogen. By agitation of a small portion of air with a large quantity of water, the oxygen may even be entirely abstracted, while the greater part of the nitrogen remains unabsorbed. Hence all water exposed to the atmosphere holds air, chiefly oxygen, dissolved, and it is difficult to expel this air from it completely.

Atmospheric air is, from its chemical powers, an important agent in many chemical and natural processes. It equalizes temperature over the globe, and distributes water. It sustains life in respiration, and is necessary in the process of vegetation. And by its chemical action it slowly effects changes in the greater number of substances which are exposed to it.

An interesting subject, but one extremely obscure, relates to the natural processes by which the purity and uniform composition of the atmosphere are preserved. By respiration, combustion, and other chemical changes going on at the surface of the earth, it is suffering constant changes; its oxygen is consumed, and carbonic acid and other gases are communicated to it. How are these changes counteracted so as to preserve the atmosphere of uniform

composition? At one time it was imagined, that the vegetable kingdom performed this important function; growing plants absorbing, it was supposed, carbonic acid gas by their leaves, and exhaling oxygen gas. The two tribes of animated beings thus stood opposed to each other in their relations to the atmosphere, and this presented an admirable view of adjustment in the economy of nature. There is, however, much reason to doubt of the facts on which the opinion rests, and, from more recent investigations, it appears even, that except when under the direct action of the rays of the sun, vegetables, like animals, consume oxygen, and form carbonic acid. There must therefore be other processes by which the changes in the atmosphere are regulated, and its purity restored; and these are at present very imperfectly traced.

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## CHAP. IV.

### OF THE CHEMICAL AGENCY OF OXYGEN IN ITS PURE FORM, AND AS IT EXISTS IN ATMOSPHERIC AIR, AND OF ITS GENERAL CHEMICAL RELATIONS.

**T**HE attractive power of oxygen towards other bodies is more extensive than that of any other chemical agent, and the history of its combinations forms perhaps the most important part of chemical science. The agencies of this element admit of some general observations; and as they are exerted by it both in its pure form, and as it exists in atmospheric air, I consider these observations as best placed after the history of the atmosphere. They form the subject of the present chapter.

The most general phenomenon attending the combinations of oxygen, is the evolution of heat and light. This constitutes the operation of Combustion or Burning, the theory of which is first to be explained.

The phenomena of combustion, and the distinction of bodies into combustible or inflammable, and incombustible or unflammable, are sufficiently familiar. The latter, when exposed to heat, have their temperature raised proportional to the degree of heat applied; but when this is withdrawn, the temperature falls, and they return to their former state. Combustible bodies, on the contrary, when sufficiently heated, begin of themselves to emit heat: this

is also accompanied with an evolution of light; and while these changes proceed, the body appears to be consumed, or at least it is converted into matter, which is no longer inflammable. It is this emission of heat and light, with an apparent waste of substance, or change of properties, which constitutes the process of Combustion.

To explain these phenomena, Stahl, following some views which had been suggested by Becher, with regard to the nature of combustible bodies, and the theory of combustion, supposed that inflammables contain a common principle, the matter of heat and light, Phlogiston as he named it, on which their inflammability depends; that the disengagement of this gives rise to the sensible phenomena of combustion, and that to its evolution the loss of inflammability is owing. He farther established, in conformity to these views, an important fact, that inflammability may be restored to the unflammable product, by heating it with another inflammable substance,—a change which he ascribed to the transfer of the inflammable principle, from the one to the other.

This hypothesis appearing to afford a satisfactory explanation of the phenomena, was universally received, and, for a considerable period, no doubt was entertained of its truth. In framing it, however, Stahl had not attended to the influence of the air in combustion: even before his time, this had been demonstrated, and the nature of it in some degree ascertained, by the experiments of Mayow and Boyle, which in particular had shewn, that the admission of the air is indispensable to burning, and that it suffers diminution during the process. These facts the doctrine of Stahl did not explain. It had farther been ascertained, that some bodies, instead of losing, gain weight in burning,

—a fact inexplicable on the supposition that combustion consists merely in the disengagement of a principle from the burning body.

Various attempts were made to solve these difficulties, but with little success; and the discoveries which were soon after made of the chemical agencies of the elastic fluids, proved still more clearly the deficiency of the original doctrine. It was observed, that combustion proceeds more rapidly in oxygen gas than in atmospheric air; and it was farther shewn by accurate experiments, that when it is carried on in atmospheric air, the volume and weight of the air are diminished, and the residual air is incapable of supporting that process,—changes which were farther proved to be owing to the consumption of oxygen. These facts led to different views. While the greater number of chemists laboured to reconcile them with the system of Stahl, two French chemists, Bayen and Lavoisier, considered them as leading to the subversion of the hypothesis. Bayen had observed, that from the calces of metals, as they were named, a large quantity of elastic fluid is given out on exposing them to heat with charcoal, or even with regard to some of them to heat alone, the metal being at the same time reduced to the metallic form; whence he concluded, that the metal owes its calcined state, not, as the system of Stahl supposed, to the loss of phlogiston, but to its combination with this air. Lavoisier had at the same period traced still farther the agency of the air in combustion. He demonstrated, what in part indeed had been shewn by former chemists, though it had never been much attended to, that its volume is diminished during this process, the diminution ceasing when it proceeds to a certain extent; that the substance in burning increases in weight, and that

from the product of the combustion, an elastic fluid may be obtained. The views suggested to him by these experiments, he gradually extended and strengthened by new researches. He at length established the simple principle, that combustion is merely the combination of oxygen with combustible bodies. And availing himself of the discovery of Black, that a large quantity of latent caloric is peculiar to a body in the aëriform state, he farther inferred, that the heat produced in burning is not derived from the combustible matter, but from the oxygen gas. The facts which had been established partly by his own researches, partly by those of others, he combined and drew from them the legitimate conclusion: he rejected an established system which commanded the assent of the greater number of his cotemporaries, and he succeeded in establishing the theory he advanced.

This theory rests on the following general facts: 1<sup>st</sup>, The presence of oxygen is indispensable to combustion: this is proved by a combustible body being incapable of being kindled *in vacuo*, or in any air which cannot afford to it oxygen; or, if kindled, it is immediately extinguished in any of these situations: while, if it be placed in pure oxygen gas, its combustion is more vivid than in atmospheric air. 2<sup>dly</sup>, The oxygen present is always consumed, as is proved by the diminution of volume and abstraction of oxygen which attend combustion in atmospheric air: hence, too, a burning body, when confined in a certain quantity of air, burns only for a limited time, that is, until the oxygen present is consumed; while, in the same quantity of oxygen gas, it continues to burn much longer; the diminution of volume too is in this case greater, and were the oxygen gas pure, and could the process



be carried on, the whole of the oxygen might be consumed. *3dly*, In every case of combustion the combustible body increases in weight, an increase equal to the weight of the oxygen which disappears: this increase of weight indeed is not always apparent; on the contrary, it often appears that the weight is diminished, or even that the body is entirely consumed; but this is owing to the product being one existing in the aëriform state, and therefore not evident to the senses: if obtained, however, and weighed, it is found to exceed the weight of the combustible body; and in every case of this kind, as well as where the product is a concrete substance, and of course more easily weighed with accuracy, the increase of weight is found exactly equal to the weight of the oxygen gas, which, during the combustion, had combined with the combustible body. *Lastly*, The oxygen which has disappeared during the process of combustion, can always be recovered from the substance formed by the process: it cannot always indeed be obtained in a pure form, for the affinity by which it is retained combined with the combustible body, is in general too powerful to be overcome by the mere application of heat, but it can always be procured by exposing the substance formed by the combustion to the action of another inflammable body, having a stronger attraction to oxygen; the oxygen is transferred from the former to the latter, and the substance which we know to be formed from that substance combined with oxygen is obtained; the quantity of this new product indicates the quantity of oxygen transferred, and this always corresponds with the quantity which had originally been consumed in the combustion. All these facts have been ascertained by experiments of great accuracy, and they establish the conclusion,

that combustion consists in the combination of oxygen with combustible bodies: These bodies are substances having an attraction to oxygen: And the products of combustion are compounds of them with this principle.

This combination, like other cases of chemical action, is influenced by temperature: in general, heat requires to be applied to cause it to commence, the evolution of caloric from the combination itself being then sufficient to enable it to proceed. The heat operates by diminishing the cohesion of the combustible body which opposes the combination, and the degree of it will be regulated by the force of that cohesion, and the strength of the affinity between the oxygen and the combustible matter. In inflammable elastic fluids, the elasticity operates as an obstacle to the combination: this is overcome by a high temperature: the operation of which, in producing this effect, I have already endeavoured to explain, (page 50). Grotthius has shewn, that the combustibility of the inflammable gases is considerably dependent on their density, so that a mixture of any of them with oxygen gas, if rarefied to a certain extent, either by heat or by the air-pump, is not inflamed by the electric spark; which kindles the mixture easily in a denser state. Hence bodies may be very inflammable under great pressure, the inflammability of which is weak, or even not apparent in a rarefied atmosphere: and in mixtures of different inflammable gases with atmospheric air, there will be a certain degree of density within which the mixture only can be inflamed.

From the facts thus established with regard to combustion, it remains to explain the phenomena which attend it,—the evolution of heat and of light.\*

With regard to the origin of the heat in burning, the

popular notion appears at first view self-evident,—that it is derived from the burning body. It is more or less hot; no other agent appears to be concerned; and it appears nearly an incontrovertible conclusion, that the body, the temperature of which is thus elevated, is the source of the caloric by which the elevation is produced. It is accordingly the conclusion which was received in the earlier hypotheses of Becher and Stahl.

The discovery of the influence of the air in combustion, however, invalidates the apparent strictness of the reasoning whence this conclusion was drawn; for, when it is established that combustion is not merely an affection of the combustible body, but is the result of its combination with a portion of the air, it is obvious, that the heat may, with as much probability, *a priori*, be supposed to be derived from the one as from the other. Whether it proceed from the combustible matter, or from the oxygen gas, it must be evolved at the surface where the combination proceeds, that is, at the surface of the burning body: this body is apparent to the senses, while the gas being invisible escapes observation; but still the caloric given out by the gas, and communicated to the substance in the act of combination, may be the cause of its elevation of temperature.

When it was farther ascertained, as was done by the discovery of Black, that æriform substances contain a large quantity of caloric peculiar to their æriform state, it became even the more probable opinion, that the caloric evolved in combustion is derived from the oxygen gas, which in that process generally passes into a more dense, and often indeed into a concrete form. This accordingly was the first modification of this opinion that was pro-

posed, the heat produced being supposed to be the latent caloric peculiar to the oxygen in its aërial form.

Another view of the subject, or rather a different mode of expressing it, was proposed by Lavoisier. He regarded caloric as existing in bodies, and especially in those in the aëriform state, in a state of chemical combination, and supposed it to be disengaged in combustion from the oxygen gas, in consequence of the superior affinity of the combustible body to oxygen.

Crawford gave the explanation under a form less hypothetical, and more directly inferred from experiment. The general fact had been demonstrated, that different bodies at the same temperature contain different quantities of caloric,—a fact expressed by saying, that they have different capacities for heat. Irvine had farther shewn, that the capacity for heat is often changed by chemical combination. It occurred to Crawford, that such a change might happen during combustion, and, if it did, might give rise to the evolution of heat which attends the process; for, if the capacity be diminished, in other words, if the capacity of the compound resulting from any combination be less than the mean of the capacities of its constituent parts, a portion of caloric must be rendered sensible, or produce an elevation of temperature. This led to an extensive experimental investigation, whence were established the general facts, that the capacity of oxygen gas for caloric is uncommonly large, that the capacities of combustible bodies are comparatively small, and that the capacities of the substances formed by combustion, though superior to those of combustible bodies themselves, are inferior to the mean of these and of oxygen gas. Hence from this diminution of capacity produced by the combi-

nation of oxygen with combustible bodies, an elevation of temperature must attend the combination, and the caloric producing this must be derived from the oxygen gas, not from the combustible matter. In different bodies, the difference in the proportion between the capacities before and after combustion are different, and hence the quantities of caloric evolved are extremely various.

It is not difficult to determine which of these explanations is to be preferred. Crawford's involves no hypothesis; and if the experiments by which the capacities are determined be correct, or even be approximations to accuracy, it is what every philosophical theory ought to be, the expression of general facts. Much care was bestowed by Crawford on the investigation, and the results appeared entitled to full confidence, or, at farthest, to be liable to errors affecting not the principle, but merely the estimation of the quantities of caloric evolved.

Lately, however, experiments have been made, which have afforded a very different estimate of the capacities of oxygen and other aerial fluids from those of Crawford, and which, if correct, overturn his doctrine. These are the experiments of Berard and Delaroche, which I have already noticed, (page 150). Instead of the large capacity assigned by Crawford to oxygen gas, they state it as inferior to that of the greater number of elastic fluids, both combustible, and the products of combustion. Its capacity, for example, compared with that of carbonic acid, is as 0.9765 to 1.2383 estimated by volume. Now, as oxygen gas is converted into carbonic acid gas by the combustion of charcoal, without any change of volume, there ought, according to this estimation, on the doctrine of capacities, to be a diminution instead of a rise of temperature,

(for the charcoal cannot be supposed to afford so large a quantity of caloric as is necessary to change this result,) and at least what heat is extricated cannot be derived from the oxygen gas.

I have already remarked, that there is still some room for doubt with regard to the superior accuracy of these results, compared with those of Crawford's experiments; and it is possible at least, that if in the latter the capacity of oxygen gas is stated too high, it may, in the former, be stated too low. The relations these chemists assign in the capacities of the gases, are at variance with a general result established by a very strict and extensive correspondence in the capacities of bodies, which, from existing in the solid or liquid form, are capable of being ascertained with more accuracy,—that the capacities of the products of oxidation are uniformly superior to those of their inflammable bases, a result which of itself, too, seems to shew that oxygen has that kind of relation to caloric whence a larger quantity of this power is requisite to produce elevation of temperature, while inflammable substances are in this respect the reverse. And these general facts, less liable to fallacy than the estimation of the capacities of the aerial fluids, are favourable to the principle on which the origin of the heat in combustion has hitherto been explained. Some other analogies, too, confirm it.

There is another point of view, however, under which this subject may be considered. The effects of voltaic arrangements have clearly shewn, that certain states of electrical action prove a source of heat; and particularly when the two electricities are discharged so as to neutralize each other, very intense heat is excited, and this even for an unlimited time: this cannot be accounted for from any

change of capacity. Now, there is some reason to suppose, that changes in the electrical states of the particles of bodies are often connected with chemical combination, though they may not always be easily traced; and if these do occur, they may, in conformity to this law, prove a source of heat, independent of any change in the capacities of the bodies which combine. And as combustion is a rapid and very intimate combination between substances having very energetic affinities, such changes, if they occur at all, are not unlikely to happen in this process.

If it shall appear from farther investigation, that the elevation of temperature in combustion cannot be accounted for from the changes of capacity found by experiment to take place, such a cause as this may, with probability, be assigned as contributing to the effect; but, in the present state of our knowledge, we have no sufficient grounds from which we can even infer the certainty of its operation, much less trace how far it modifies the action of the other; nor is it by any means clearly proved, that the evolution of heat in chemical action is inconsistent with the doctrine that it may be derived from changes of capacity, though arguments, in support of this conclusion, have been often urged, arising from misconception of the subject.

The origin of the light in combustion is of difficult explanation. Lavoisier had supposed it to be derived from the oxygen gas, but without any conclusive evidence; for it is obvious, that the admission of the fact, that the caloric is evolved from this gas, is no proof that the light has the same source; at least without the assumption that these two principles are the same.

We have perhaps no very decisive evidence, that the light is derived from the combustible body; still there are

some facts which appear to render this the more probable opinion, admitting at least that light is subject to chemical affinities, and enters into chemical combinations. Thus, light is often evolved, when oxygen is transferred from one inflammable to another, and as the oxygen in its first combination has parted with its light, if it contained any, the light evolved in the second combination must be supposed to be derived from the inflammable body. Another fact, more conclusive, is, that an evolution of light attends the combination of inflammable substances with each other, of which we have a striking example in the combination of sulphur with metals. This appears to prove that light exists in these bodies, and as we have no similar proof of its existence in oxygen gas, it follows as the more probable conclusion, that the light evolved in combustion is derived from the combustible body. At the same time, it is to be remarked, that with regard to principles so subtle, our conclusions must in the present state of chemistry be uncertain; and the production of intense light by ignition and by galvanism, without our being able distinctly to assign its origin, proves sufficiently that we are imperfectly acquainted with the chemical relations of this power, and that it is by hypothesis only that we consider it as subject to those laws of combination which are applied to ponderable substances.

Very different quantities of light are given out by different combustible bodies in burning; in general, the illumination is greatest from those which are in the state of vapour while burning: this is not, however, strictly necessary, some substances which remain fixed, as phosphorus or iron, giving very intense light. The constitution of the light emitted with regard to the different coloured rays, is



also different in different bodies, some in burning giving white, others differently coloured light. This appears to be very much connected with the temperature which accompanies the combustion. Those which burn with a low heat, as sulphur or ardent spirit, in general emit the blue or purple rays most copiously; those which burning produce a greater elevation of temperature, as charcoal, give the red rays; and where the temperature is high, and the combustion rapid, all the rays are emitted so as to constitute white light.

Besides combustion, there are other cases of the combination of oxygen more complicated, in which, after having been combined with one body, it is transferred from it to another.

Such is the operation of Deflagration. When an inflammable substance is mixed with nitre, on kindling the mixture, a very rapid combustion, attended with the disengagement of much heat and light, takes place, and this independent of any action of the air. The theory of the operation is, that in nitre a large quantity of oxygen exists in a concrete form, this salt consisting of nitric acid and potash, and this acid being composed of oxygen and nitrogen. These elements are not retained in union by a strong attraction; hence, when exposed to heat they separate, and, in deflagration, the oxygen being presented to the inflammable substance, combines with it rapidly, and causes it to burn. The nitrogen gas assumes the elastic form, mixed frequently with an æriform product from the combustion. There is some difficulty in accounting for the high temperature produced by deflagration. Oxygen existing in the elastic form probably has a large capacity

for caloric, and suffering a diminution of capacity in the combinations into which it enters, the temperature must be elevated. But existing in nitre in a concrete state, it is not to be presumed that its capacity will be equally great. In passing therefore into a new state of combination, there cannot be a diminution of capacity to the same extent, and hence there must be less caloric evolved. In some cases even of deflagration, the compound which the oxygen forms with the combustible body exists in the aëriform state; and reasoning from analogy, it must require more caloric to produce in it a given temperature than the nitre itself. This difficulty perhaps is not easily entirely removed. It may be remarked, however, what so far lessens it, that a less quantity of heat, it has been experimentally proved, is evolved from the consumption of a given quantity of oxygen by deflagration, than from the consumption of the same quantity by combustion. It is also to be observed, that when oxygen combines with nitrogen, to form nitric acid, little caloric is set free; and again, when this acid combines with potash to form nitre, there is little disengagement of heat. We thus trace the caloric in oxygen gas into the solid salt, and hence may expect it to be evolved, when the oxygen is transferred to an inflammable substance. The only difficulty is, whether the large quantity of caloric, which would thus appear to be contained in nitre, exists in it from its actual capacity; and with regard to this, we have as yet no experiments that can be considered as decisive.

The origin of the light in deflagration, must be the same as that in combustion.

From the sudden and rapid extrication of aëriform matter, which attends deflagration, a high elastic power is ex-

erted, which is farther increased by the high temperature. This is greatest when, with the gaseous matter, from the decomposition of the acid of the nitre, there is an aëriform product from the combination of the oxygen with the inflammable. This happens in the deflagration of charcoal and of sulphur, and to this the expansive power of gunpowder, which consists of these ingredients mixed with nitre, is owing. In some cases, the quantity of elastic product is so great, and the elasticity of it so much augmented by the caloric suddenly disengaged, that the mere resistance of the atmosphere gives rise to a loud noise. This forms what is named *Détonation*. It is not only produced by heat, but, with regard to some substances, by friction, or percussion.

The last general case of the combinations of oxygen to be noticed, is that where it is transferred from one body to another, without being accompanied by combustion. Thus the acids contain oxygen. In acting on an inflammable substance or a metal, they often yield this oxygen. Water, which is a compound of oxygen, sometimes affords it to other bodies; and the presence of an acid often favours this, or causes the water to be more rapidly decomposed. In all these cases, there is no great elevation of temperature, partly because the oxygen existing in these compounds has been deprived of the caloric peculiar to it in the aërial form, and partly as the substance evolved from the decomposition of the acid or the water, and which is usually gaseous, absorbs much of what would otherwise be rendered sensible. Neither is there in general any evolution of light: if evolved it is either not sensible from the slowness of the process, or it passes into combination with the base with which the oxygen had been combined.

The combination of oxygen with a body, whatever may be the phenomena attending it, is named in general Oxidation or Oxygenation, or according to the nomenclature proposed by Mr Chenevix, Oxidizement or Oxygenizement. The result of it is, the formation of compounds which possess some common properties, and agree to a certain extent in the chemical agencies they exert. Hence they admit of some general observations.

Of these compounds some have a sour taste, redden the vegetable colours, and combine with the alkalis, so as to neutralize the alkaline properties. A substance possessed of these powers is named in chemical language an Acid. There are a number of Acids, and these in general, so far as they have been analysed, contain oxygen. Hence this element is considered as the principle of acidity, from which indeed its name is derived.

Acidity, however, is not the invariable result of the combination of oxygen. Its compounds are often destitute of any acid property. It is convenient to have a term to denote this class, and in the modern nomenclature they are denominated OXIDES.

Oxides and Acids, then, are two orders, comprizing all the compounds of oxygen. Acids are distinguished by the possession of certain common properties. Oxides have scarcely any common qualities by which they are distinguished; the distinction being rather negative, or denoting that the compound has no acid power. The alkalis and earths having been discovered to be compounds of oxygen, are to be regarded as oxides, and the most distinguishing property common to them, and likewise to all the metallic oxides, is that of neutralizing the properties of acids. But there are likewise oxides to which this property does

not belong. The word oxidation or oxidizement is used, in strict propriety, to denote that combination of oxygen where the resulting compound is not an acid, but an oxide. Oxygenation or oxygenizement is a more general term, expressing every combination of oxygen.

Many substances are capable only of oxidation. Thus the greater number of the metals in combining with oxygen form oxides; nor, with one or two exceptions, can they be made to acquire any acid property. Hydrogen unites with oxygen only in one proportion, and forms water, which is not acid.

There are other inflammable substances, again, which, in combining with oxygen, form in one proportion an oxide, and in another an acid. In general, the first degree of oxygenation forms an oxide, and this, with a larger proportion of oxygen, forms an acid. There are some, however, which appear to form acids even in the first stage of oxygenation; at least their existence in the state of oxide is doubtful. But, in all those substances which, by combining with oxygen in different proportions, produce both oxides and acids, the oxide is invariably the product of the first proportion, and the acid results from the addition of a larger proportion of oxygen. In some cases, the same substance too is susceptible of different degrees of oxygenation, so as to form two acids different in their properties from each other; the one, from the larger proportion of oxygen, being usually the most energetic in its action.

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## BOOK II.

### OF WATER AND ITS BASE.

If any ponderable substance can, from general reasoning with regard to its powers, be considered as an element, water might, from the large quantity in which it exists in nature, and from the extent of its agency, claim this distinction. In nearly every system, both of ancient and modern philosophy, the elementary nature of water has accordingly been admitted as a leading principle.

The more rigorous researches of Modern Chemistry, however, establish its composition. It was observed, that in the combustion of a peculiar species of inflammable elastic fluid, water is the only sensible product; and that the quantity of it which appears is equal to the quantity of this inflammable gas and of the oxygen gas which are consumed in the combustion. And again, when substances having a strong attraction to oxygen are made to operate on water, they are found to have received this principle; a portion of the water disappears, and the inflammable gas is produced. It follows, from these facts, that water is a compound of these two gases, and though some doubts have been suggested with regard to this conclusion, it has all the support which the evidence of chemical induction can give. The inflammable gas is named Hydrogen, and its history precedes that of water.

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## CHAP. I.

### OF HYDROGEN.

**H**YDROGEN, the inflammable base of water, exists when uncombined in the aerial form. Being disengaged in various common chemical processes, and from its property of inflammability being more easily recognised than the other elastic fluids, it was known, though imperfectly, to the older chemists. Cavendish first clearly demonstrated its distinct existence and characteristic qualities, under the name of Inflammable Air. It received the denomination of Hydrogen from being regarded as the base of water.

It is always obtained from water, subjected to the action of substances which attract oxygen. Thus, if watery vapour be passed over iron at a red heat, hydrogen gas is procured, and the iron is oxidated. If the resulting affinity of an acid be introduced, its production is more rapid, and takes place at a natural temperature. This is the process, therefore, generally followed. One part of iron or zinc in fragments, is put into a bottle with a bent tube adapted to it, and two parts of sulphuric acid, diluted with five times its weight of water, are poured upon it; hydrogen gas is rapidly disengaged. The agency of the acid in promoting the decomposition is obscure, but, so far as any explanation can be given, it may be classed as an example of what Berthollet names Resulting Affinity; the acid, the metal, and the oxygen of the water, exerting mutual forces

of attraction, whence they combine, while the hydrogen, separated from its combination with the oxygen, assumes the elastic form.

Hydrogen gas is the lightest of the elastic fluids, and the lightest substance therefore whose gravity we can ascertain. When collected over water, it is about 10 times lighter than atmospheric air. When freed as much as possible from the vapour it holds dissolved, it is nearly 13 times lighter, or the specific gravity of atmospheric air being 1000, that of pure hydrogen is 0073. The weight of 100 cubic inches is 2.230 grains. It is from this levity that it is employed in the construction of balloons. When free from water it is inodorous, but when humid it has a slight smell.

Inflammability is the property which, next to its great rarity, eminently distinguishes hydrogen. It kindles on the approach of an ignited body when in contact with the air: if previously mixed with twice its volume of atmospheric air, it explodes when kindled; with oxygen gas its explosion is still more violent. The state of dilatation affects the facility with which it is kindled, and if its mixture with atmospheric air be under a pressure four times less than that of the atmosphere, it does not inflame, either from the contact of an ignited body, or the electric spark.

From this inflammability hydrogen gas has been applied to the purpose of eudiometry, a given volume of it being introduced into the tube, Fig. 22. with a measured quantity of the air submitted to trial, and the mixture being inflamed by the electric spark. The diminution of volume indicates the quantity of oxygen that had been contained in the air, 100 measures of oxygen combining with 200 measures of hydrogen: the third part of the diminution of



volume gives therefore the quantity of oxygen by volume. The proportion of hydrogen employed, ought to be always a little greater than what may be necessary to saturate the quantity of oxygen in the air submitted to trial; as thus the error of any part of the oxygen escaping combination is more effectually guarded against. In analyzing atmospheric air, 100 measures may be mixed with 50 of hydrogen; the total diminution will be 63 by volume, and the third of this gives the proportion of oxygen at 21. This method has the advantage of great delicacy, from the very considerable reduction of volume: it appears also to be sufficiently accurate; it requires no corrections for variations of atmospheric pressure or temperature; and others are preferred to it only as being rather less difficult in the execution.

Hydrogen gas proves fatal to animal life when respired, apparently, however, not by any positively deleterious power, but merely by excluding oxygen; hence it can be breathed for a few inspirations; and when diluted with a portion of atmospheric air, can be breathed longer with safety. It does not, like some of the other elastic fluids, prove noxious to vegetable life; some plants even absorb it; and there are observations which appear to prove, that it can, to a certain extent, supply the place of light in supporting vegetation.

Hydrogen gas is not sensibly absorbed by water, at least unless the water has been previously freed from the atmospheric air it holds dissolved; 100 cubic inches of it then take up, according to Henry's experiments, 1.5 of the gas; by applying strong pressure, the water may be made to absorb one-third of its volume.

Hydrogen enters into chemical combinations with inflammable substances, sulphur, phosphorus and carbon;

it also combines with some of the metals. With oxygen it forms water, with nitrogen ammonia; and it is an abundant ingredient in the vegetable and animal products. It is disengaged by some natural processes, though not pure. Thus, holding carbon dissolved, it rises sometimes from stagnant water in which vegetable matter is diffused; and in a similar state of composition it is collected in mines, forming what has been named Fire Damp.

The recent discoveries in chemistry suggested some speculations with regard to the nature of hydrogen. Quicksilver when submitted to galvanic action in contact with ammonia, suffers changes analogous to what it would suffer from the addition of metallic matter. As ammonia is a compound of hydrogen and nitrogen, the conclusion was adopted that it is decomposed in this experiment, and that the metallic matter supposed to be communicated to the quicksilver must be derived from its elements hydrogen or nitrogen. The former being inflammable, may be supposed, with more probability, to be allied to metals, and the results therefore were supposed to afford some ground for the conclusion, either that its gravitating matter is metallic, in other words, that hydrogen is a metal in the gaseous form, or that it is a metal in some state of combination, perhaps in an oxidated form. Subsequent researches, however, have added no confirmation to this conjecture, and even lead to a different view, as is afterwards to be stated, of the nature of the change which the quicksilver suffers in the above experiment. It is only on hypothetical and vague speculations that the farther conjecture has been advanced, that hydrogen may be the common principle of inflammability, and as such opposed in its chemical relations to oxygen.

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CHAP. II.

## OF WATER.

THE composition of water has been inferred both from analysis and synthesis. When hydrogen gas is burnt, an operation in which oxygen is combined with it, water is the only sensible product; and when water is acted on by substances capable of attracting oxygen, these are oxidated, the water disappears, and hydrogen is evolved. From these facts, the conclusion was drawn nearly at the same period by Cavendish and Watt, that water is a compound of hydrogen and oxygen; and the experiment, of forming water by burning hydrogen gas, was executed by the former philosopher on a considerable scale. It has since been often repeated with every attention as to the proportions and the accuracy of the results.

This was necessary, not only from the importance of the question in its relations to chemical theory, but also as some circumstances connected with the experiment required to be elucidated. In particular, it was observed, that an acid is frequently formed with the water; and some were disposed to conclude, that this is the real product, and that the water is only adventitious, being the moisture deposited, which had been held dissolved by the gases. More minute examination, however, discovered the origin of this acid. It was found to be generally the nitric: this

acid is a compound of oxygen and nitrogen, and had therefore been formed from nitrogen which had been mixed with the gases, and from which indeed it is difficult to procure them entirely free. Sometimes the acid appeared to be the carbonic, and this had obviously been derived from a small portion of carbon held dissolved by the hydrogen, derived from the materials from which it had been obtained. When these sources of fallacy are guarded against, the water formed in the combustion is perfectly pure, and the weight of it amounts exactly to the weight of the hydrogen and oxygen gases consumed. This has been established by repeated experiments, made on a large scale, and with the greatest care.

The composition of water has also been established by analytic experiments. When transmitted over iron at a red heat, the iron is oxidated, and hydrogen gas is disengaged. And it has farther been proved, that the quantity of hydrogen, added to the increase of weight which the iron gains by its oxidation, corresponds with the quantity of water which disappears.

The action of electricity affords a mode of resolving water into its constituent gases, and of combining these again so as to reproduce it, which is very conclusive in establishing its composition. When an interrupted electrical discharge is transmitted by wires, placed at a short distance, through a column of water, there is a production of æri-form fluid; and when from repeated discharges this has accumulated in sufficient quantity to be examined, it is found to consist of oxygen and hydrogen gases: hence, when the electric spark is taken in it, it disappears with inflammation; the two gases being combined, and water formed. The experiment, as a proof of the composition of water,

is so far satisfactory, as the results are obtained without the intervention of any other ponderable matter.

The action of electricity, in the form of galvanism, affords similar results, connected also however with peculiar phenomena, which require to be stated more particularly, as it is from them that doubts have been suggested, whether the theory with regard to the composition of water is just.

If in a quantity of water in a glass tube a platina wire connected with the positive side of a galvanic battery, and another similar wire from the negative side be inserted, on bringing the extremities of the wires to the distance of about half an inch from each other, a stream of gas arises from each, and this continues while the galvanic action is kept up, until, by the accumulation of elastic fluid, the water is depressed beneath the extremity of the upper wire. This aerial fluid is found to be a mixture of oxygen and hydrogen, in the proportions which form water, and by transmitting the electric spark through it, it is again converted into water.

In this experiment a phenomenon occurs which appears at first view singular. If the evolution of elastic fluid arise from the decomposition of water, it might be expected that the elements must be evolved together, and that of course a stream of oxygen and of hydrogen gases shall arise from each wire. On making the experiment, however, so that the gas from the wires shall be obtained separate, as is done by inserting each in a separate tube, either placed in the same vessel of water, or connected by a humid conductor or by the interposition of certain liquids, it is found, that the gas from the one wire, that connected with the positive side of the galvanic battery, is oxygen, that from

the other or negative side is hydrogen, and each is perfectly pure, if care has been taken to free the water from the atmospherical air it holds dissolved. The elements of the water are evolved therefore at separate, and even at distant points; and if this arise from its decomposition, the question that obviously presents itself is, what becomes of the oxygen at the wire where the hydrogen is evolved, and what becomes of the hydrogen where the oxygen is given out?

To solve this question, various hypotheses were proposed: it was soon established, however, that the phenomenon is not peculiar to water, but is merely a case of the general law, (already illustrated page 229), established by the researches of Berzelius and Hisinger, with regard to the decomposition of all chemical compounds, and illustrated by Grotthius particularly with regard to water,—that when compounds are submitted to the action of galvanic electricity, their elements separate, some having such a relation to the electric states as to be collected around the positive pole, others being collected around the negative pole; oxygen and acids belonging to the former class, hydrogen, and in general inflammable substances, as well as alkalis and earths, belonging to the latter. When water, therefore, is submitted to the action of galvanic electricity, it suffers decomposition, its oxygen is attracted to the positive wire, and if this is a metal not susceptible of oxidation, it there assumes the elastic form; its hydrogen is at the same time attracted to the negative wire, and as it can neither penetrate nor combine with the metal, it also assumes the elastic state. The mode of decomposition is not apparent, but it may arise, as has been already remarked, from the electric states being communicated to the elements

of the water, and the attractions exerted in consequence of this at each pole overcoming their mutual chemical attraction, whence will arise their separation and their transfer to the respective poles, the element which becomes negative passing to the positive side, and that which becomes positive passing to the negative side. In this case the middle particle of water between the two wires may be that which is decomposed, or a particle at each extremity may suffer decomposition, and either a series of successive decompositions and recompositions may be established through the whole interposed fluid, or the element not evolved at each wire may move, by the attractive and repulsive powers operating upon it, to the opposite side.

At one time a different view of this subject was proposed. Water, it was remarked, may not be a compound, but a simple body, assuming the forms of oxygen and of hydrogen according to its electrical states. When rendered positively electrical, it will form hydrogen gas; when in the opposite or negative state, it will constitute oxygen; and when brought within the sphere of action in these forms, the two electrical states will be subverted, the equilibrium established, and water will be reproduced. The possibility of such an hypothesis may be maintained, but it has nothing peculiar for its support. Were water the only substance suffering such changes when submitted to galvanic action, this would afford some grounds for such a conclusion; but all compound substances suffer changes equally important; they appear under the form of new substances, or are converted into what we regard as their constituent principles. To consider these principles as the compound in different electrical states, would be an extension of the theory extravagant and absurd, yet there is no reason why it should be

limited to water, since there is nothing peculiar in its apparent production or decomposition. And the result of an experiment which was at one time stated by Ritter in support of it, that of oxygen and hydrogen being separately evolved from the galvanic wires, when they are placed even in separate portions of water, connected only by a substance capable of conducting electricity, as sulphuric acid or a metallic wire, is a mere deceptive appearance, the connecting matter becoming at its two extreme surfaces, in contact with each portion of water, electrical by induction, and these giving out the oxygen and hydrogen corresponding to the portions evolved at the galvanic wires.

It was at one time supposed, that in the decomposition of water by galvanism, there is a formation of new products: a portion of acid frequently was observed to be formed at the positive wire, and of alkali at the negative wire. The origin of these was traced by Mr Davy. They are in general derived from the small portion of saline matter which water holds dissolved, and from which it is not even perfectly freed by one distillation, the acid of this being attracted to the one wire, the base to the other; and as these attractive powers are so strong, the most minute quantities are rendered sensible. From the same circumstance, even the containing vessel is sometimes acted on; and the atmospheric air held dissolved by water has some influence, its nitrogen, by combining with the nascent oxygen at the positive pole, forming nitric acid, and combining in like manner with the nascent hydrogen at the negative pole, and forming ammonia. But when these sources of fallacy are avoided, the water remains pure to the end of the experiment, and is resolved into oxygen and hydrogen alone.



There is some difficulty in assigning the precise proportions of the elements of water. They have usually been stated in round numbers at 85 parts by weight of oxygen, and 15 parts of hydrogen. Experiments, however, by different chemists have given other proportions, from 13 of hydrogen to 15.7. It appears also from the observations of Gay-Lussac and Humboldt, that in fixing the proportions by weight, the due allowance has not been made for the portions of hygrometric water which the respective gases hold in solution previous to combination, and with this correction they shew that the proportions, from the most accurate experiment, are 87.4 of oxygen, and 12.6 of hydrogen. The proportions of the two gases by volume appear to be 100 of oxygen, and 200 of hydrogen, which are conformable to the law that gases combine in very simple proportions, estimated by volume.

Water, as a chemical agent, has qualities extremely peculiar. It affords the example of an inflammable base saturated with oxygen, forming a product which has no acidity. Besides this, though its affinities are extremely numerous, they are seldom energetic; and hence in general it combines with bodies, without materially changing their qualities, and by communicating fluidity to solids, without modifying much their chemical relations, favours their mutual actions. From recent researches, however, it appears in some cases to exert more important chemical powers.

It is tasteless, colourless, and inodorous. It passes to the solid state at  $32^{\circ}$  of Fahrenheit, and in doing so crystallizes, spiculæ shooting out at a certain angle, and of a prismatic form: by the continuance of the congelation, the vacuities are filled up, but the mass remains transparent, and is hard and brittle. In congealing, there is, as has

been already stated, an enlargement of volume, and this expansion even takes place previous to the congelation, during the reduction of temperature, for six or eight degrees, the greatest density of water being about  $40^{\circ}$ . In the act of freezing, too, the greater part of the air which the water holds loosely dissolved is expelled.

Water passes into vapour when exposed to the atmosphere at any natural temperature, and even ice evaporates, as is proved by its losing weight when suspended in the air. The transition into vapour is promoted by heat; at  $212^{\circ}$ , under a medium atmospheric pressure, water boils. Its vapour at this temperature is permanent, transparent, and invisible; when condensing, it becomes, from the approximation of the particles, opaque. It occupies 1800 times the space which it fills when in the state of water, and has a specific gravity to that of atmospheric air at the same temperature; according to Tralés, as 0.6896 to 1.0000, 100 cubic inches weigh 21 grains. It exerts a great degree of elastic power, and its elasticity increases in a high ratio by elevation of temperature.

Water absorbs the aerial fluids, but in quantities very different, according to the force of attraction which it exerts towards them. Of some of the acid gases, it absorbs many times its own volume; of others the quantity is so inconsiderable as not to be very perceptible, unless ascertained by an apparatus peculiarly adapted to shew the result. The quantities absorbed are greater as the temperature is low, down to freezing, when the cohesion of the solid, weakening the affinity, the aerial matter is expelled. They are also augmented by pressure; and, according to a law stated by Dr Henry, as the result of his researches on this subject, "Water takes up in all cases, under equal

circumstances of temperature, the same volume of condensed gas, as of gas under ordinary pressure." To whatever degree of density, therefore, the elastic fluid is brought by pressure, the same volume of it is still absorbed; and hence, by increasing pressure, a large quantity of the solid or gravitating matter of the gas may be forced into the water. It is singular, that water thus impregnated by pressure with large quantities of the gases, which, under the mere pressure of the atmosphere it absorbs sparingly, does not suffer much change in its qualities. 100 cubic inches of water, previously freed from air by boiling, absorb, according to Dr Henry, under a common atmospheric pressure, 3.5 of oxygen gas, 1.5 of nitrogen gas, and 1.5 of hydrogen gas. According to Gay-Lussac and Humboldt, the proportion of oxygen is considerably larger, that of hydrogen rather less.

This absorption of gases by water, so far as regards those which require pressure to cause their absorption in any sensible quantity, has been supposed by Mr Dalton to be a mere mechanical effect, the gas being forced as it were into the interstices of the water by the pressure applied. It is rather to be regarded, however, as arising primarily from the affinity exerted by the water to the particles of the aëriform fluid. This is counteracted by the elasticity of the gas, and not being strong it cannot operate with much effect. Pressure counteracts this elasticity, hence lessens the resistance opposed to the combination, and, operating like reduction of temperature, causes a larger quantity to be absorbed. We accordingly find, that in those cases where the exertion of an affinity by the water to the gravitating particles of the gas is undoubted, as in the example of muriatic acid gas, pressure

is equally effectual in promoting the absorption : and also what is in conformity to this view, that even in those gases the absorption of which is inconsiderable, the quantities absorbed are different under the same pressure,—a difference which can only be ascribed to the different forces of affinity exerted to them by the water.

There are some important facts with regard to the relations of water to the aerial fluids in their absorption. Thus, from the affinities it exerts to all of them, however weak, if it be agitated with a mixture of two or more gases, portions of both will always be absorbed, the same as if they were presented to it separately in their proper density; the quantity therefore being greatest of that which separately is most largely absorbed by water. Or, if water has been previously impregnated with one gas, on agitating it with another, a portion of the latter will be absorbed, and a portion of the former displaced. Hence, as water usually contains a portion of atmospheric air, in exposing any gas to an extensive surface of it, and still more in agitating any gas with it, while a quantity of this is absorbed, a portion of the air the water holds dissolved will be separated, and added to the residual gas, whence frequently sources of error have arisen in chemical experiment; oxygen gas, for example, if kept in a jar surrounded with water exposed to the air, will soon have an intermixture of atmospheric air; and indeed all gases long exposed in this manner have a similar intermixture from the water yielding its air.

Water which has been exposed to the atmosphere always contains portions of both of its constituent gases; but the oxygen is absorbed in preference to the nitrogen, and in considerably larger quantity. Hence by agitating

atmospheric air with a large portion of water, or passing it repeatedly through a column of water, the greater part of its oxygen is abstracted. The presence of oxygen loosely combined in water, is usually shewn by the test of sulphate of iron; the oxide of iron which is the base of this salt, attracting this portion of loose oxygen, whence becoming insoluble, it is precipitated, and forms a yellow sediment: this precipitation seems also, however, to be in part owing to the decomposition of the salt by the affinity of the water to its acid, aided by its quantity. The air expelled from river water by boiling contains, according to Gay-Lussac and Humboldt, 0.319 of oxygen; that from rain water 0.310; that from spring water, according to Henry, contains a considerable proportion of carbonic acid.

The portion of air held dissolved by water is expelled with difficulty. It is in part removed by removing the atmospheric pressure by the air-pump, by strong boiling, and by freezing, but part of it is still retained. It is rather singular too that the nitrogen appears to be retained with greatest force, the first portion of air disengaged containing more oxygen than the second; or, if through water freed as much as possible from air by boiling, and by the air-pump, an electrical discharge be transmitted, a small portion of nitrogen is disengaged, along with the oxygen and hydrogen evolved from the decomposition of water, as Dr Pearson found in his experiments. And in freezing water which had been previously freed as much as possible from air by boiling, the air disengaged is, according to the experiments of Priestley, nitrogen, especially when the freezing of the same portion of water has been repeatedly performed. Ritter, on the contrary, inferred from some experiments; that the air disengaged in the freezing of

water is oxygen, evolved from decomposition, and that ice has therefore an excess of hydrogen. According to Davy, it is atmospheric air, and the production of it does not take place in the unlimited manner which had been represented by Priestley, but ceases after the freezing has been repeated three or four times. Gay-Lussac and Humboldt found, that the air disengaged in successive portions from water by boiling contains more oxygen in the latter portions than in the first, while in freezing the oxygen is rather retained, and the nitrogen disengaged. Water melted from snow with the exclusion of the atmosphere, appears to be nearly free from air. Gay-Lussac and Humboldt, however, affirm, that it contains nearly the usual proportion of air: the water from melted ice does not contain so much. Rain water, and especially dew, have been supposed to be saturated with air.

Water is contained in all the elastic fluids, derived either from the materials from which they have been extricated, or that through which they have been transmitted. It exists in them in the state of vapour, probably weakly combined, and is capable of being condensed, in part at least, by cold, and of being abstracted by substances exerting an attraction to it. This is named Hygrometric Water or Hygrometric Vapour, and its quantity is in a great measure dependent on the temperature, augmenting however in a much higher ratio as the heat is raised, than the arithmetical progression of temperature. According to Mr Leslie, atmospheric air, absolutely humid, holds dissolved, at the temperature of  $32^{\circ}$ , the hundred and sixtieth part of its weight of water; at  $59^{\circ}$ , the eightieth part; at  $86^{\circ}$ , the fortieth part; at  $113^{\circ}$ , the twentieth, and at  $140^{\circ}$  the tenth part. In the other elastic fluids the quantity, there is every reason to believe, is the same.

Besides this hygrometric vapour, a portion of water has been supposed to exist in some gases more intimately combined, not capable of being abstracted by those methods which condense the other, and essential to their constitution.

One fact from which this has been inferred, is, that in compounds in which these gases exist in a dry state, the gas cannot be disengaged by heat unless water be supplied. This is the case with the native carbonate of barytes or of lime; and from the former, even the carbonic acid is very imperfectly disengaged by an acid, unless it be diluted with water. Hence it has been inferred, that water is essential to the constitution of carbonic acid gas; but it is more probable that the operation of the water is not on the gas, but on the base with which it is combined, favouring its disengagement by the attraction it exerts to that base.

The existence of water in intimate combination, in one gas, muriatic acid gas, in considerable quantity, is more unequivocally established, as is to be stated under the history of that acid. But this arises from nothing peculiar to this substance as an elastic fluid; it is the consequence merely of its powerful affinity to water; and the existence of the compound of the real acid with water in the gaseous form depends merely on its relation to temperature, as does the existence of other similar compounds in the liquid or solid form.

Hygrometric vapour is abstracted from gases by a number of substances which have a strong attraction to water, as by dry potash, by lime, or by sulphuric acid. Gay-Lussac and Thenard discovered an agent which abstracts it still more powerfully, and affords a more delicate test by which it may be discovered, Fluo-boric acid gas. So powerful is the affinity of this substance to water, that when

presented to atmospheric air, or to any elastic fluid, containing any portion of hygrometric water, it instantly attracts, and at the same time forms with it very dense vapours. It does not however attract combined water, and hence it produces no opacity when added to muriatic acid gas, a proof that the latter contains no hygrometric vapour.

Water appears to have an important chemical relation to acids, and in this relation displays a more powerful agency than in its other combinations. All the powerful acids exert a strong attraction to it ; such as the sulphuric, the nitric, muriatic, fluoric and phosphoric ; they cannot even be obtained free from it in an insulated state, and it appears to have an important effect in their more characteristic acid properties. The facts connected with this, belong rather to the history of acids.

A very strong attraction is exerted between water and the fixed alkalis ; and it farther appears, that they always in their insulated state retain a considerable portion of it in combination, so that it cannot be abstracted from them, unless when they enter into other combinations. A similar relation exists between it and the alkaline earths.

The compound salts also always contain water, even those of them which appear altogether insoluble. The soluble salts display a stronger attraction to it ; and in those of them which crystallize, it is always retained, forming a part of the substance of the crystal. It exists too in many native mineral products, saline, or compounds of earths with each other. Even those earths and stones which it cannot dissolve, it wears away and reduces to a state of extreme division, partly by attrition, and partly by its chemical powers. Hence it acts even on glass, especially when aided by a high temperature,—a fact which at one time gave rise to the opinion that it is convertible into earth, a



portion of earth being always left when it is distilled from glass vessels.

Water, though incapable of combining with the metals, exerts a chemical action upon them, affording to several of them oxygen at the temperature of ignition; and at a natural temperature, aided by atmospheric air, oxidating or corroding others. It also combines with some of their oxides. At a high temperature it is decomposed by charcoal and sulphur, which receive from it oxygen.

Water is a solvent of many other substances. Few of the animal or vegetable products are insoluble in it, and all of them are affected by it as a chemical agent, receiving from it oxygen, or the re-action of their constituent principles being promoted by the fluidity it communicates, so as to give rise to spontaneous decomposition.

Those compounds in which water exists in intimate combination, and the properties of which it appears to modify, are named Hydrates.

From the extensive solvent power of water, it is scarcely ever met with pure in nature. Every kind of spring or river water is impregnated with saline and earthy bodies of different kinds. Spring water contains, according to Bergman, carbonate of lime, muriate of lime, and muriate of soda; river water contains carbonate of lime, muriate of soda, and each of these also sometimes a little alkali. Well-water, besides these, contains always a portion of sulphate of lime, the presence of which is the cause of the quality in waters termed *Hardness*. Rain or snow water is freer from these foreign substances, but is not perfectly pure, as it affords a trace of muriate of soda and muriate of lime. Water is freed from these substances by distillation: and for any chemical process in which accuracy is requisite, distilled water must be used.

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## BOOK III.

### OF ALKALIS AND THEIR BASES.

THREE substances possessed of certain common properties have been long classed together in chemical arrangements, under the name of Alkalis. They are soluble in water; their taste is acrid; and when applied to animal matter, they erode or dissolve it; they change the blue and purple colours of vegetables to a green, the yellow they change to a brown; they combine with oils and fats forming soaps; and they unite with the substances which belong to another class, the acids, neutralizing their characteristic properties, so that in the compound which is formed, when the due proportion is observed, the presence of the acid or of the alkali cannot, from any remaining property of either of them, be recognised. The three alkalis are named Ammonia, Soda, and Potash (or what, for similarity of termination, would be preferable, Potassa.) The first existing when uncombined in the aerial form, and being even when combined with water easily volatilized, has been named Volatile Alkali; the other two, though they are volatilized at a red heat, yet still having comparative fixity, are denominated Fixed Alkalis.

The most characteristic property of the alkalis is that displayed in their relations to the acids, their combining with them, and forming compounds in which the peculiar acid powers are neutralized. But the same property is

possessed by another order of chemical agents, the Earths ; and several of these approach even more closely to the alkalis, being soluble in water, acrid and caustic, combining with oils, and changing the vegetable colours to a green. In the leading property common to both, the analogy is even still farther extended, for the compounds of the metals with oxygen, the Metallic Oxides as they are named, are equally capable of combining with the acids, and of neutralizing the acid powers. Thus, the whole are connected into one series ; and though the alkalis, earths, and metallic oxides may be distinguished as subordinate orders, by some peculiar characters, they are still in their most important chemical relations strictly connected, and the transition is nearly uninterrupted, from the substance placed at the commencement of the one division, through those belonging to the others.

This analogy has been rendered perfect by the discovery, that the alkalis and earths are compounds of a basis of a metallic nature with oxygen ; that under this point of view, therefore, they are actually metallic oxides. The earths resembling the more common metallic oxides in many of their properties, had frequently been supposed to be metallic ; but the same supposition had scarcely been extended to the alkalis, partly as their properties are more remote from those of metallic oxides, and partly from the composition of ammonia having been discovered, and having apparently no relation to metallic matter. Mr Davy, led by the knowledge of the law which regulates the chemical decompositions produced by galvanism, succeeded in effecting their decomposition, and obtaining from them oxygen and bases having metallic properties. He submitted the earths to the same powerful instrument of analysis ; and

though their decomposition has been less perfect, it has been sufficiently so to demonstrate that they also consist of metallic bases in an oxidated state. The analogy was thus extended through the series of the earths and fixed alkalis to the oxides of the metals, proving that they are of similar chemical constitution. Ammonia alone remains insulated, and even from it, submitted to the action of galvanism, results are obtained which indicate some relation to metallic matter.

Though the alkalis, earths, and metallic oxides have been connected by these discoveries, there remain sufficient reasons to arrange them as distinct orders. The bases of the alkalis and the earths, admitting them to be metallic, are different from the common metals, both in physical and chemical properties; and except in the leading character of combining with the acids, the alkalis are very different in their qualities from the metallic oxides, and are much more active in their chemical relations. The earths approach nearer to the metallic oxides, and form the series connecting them with the alkalis.

Several of the earths, particularly barytes and strontites, approach so nearly to the alkalis in their properties, that it has been proposed to transfer them to this class. They are still, however, on the whole, more strictly connected with the other earths: and if the entire series is to be subdivided into two orders, it could not be done with more propriety, than in conformity to those already established. The alkalis may be regarded as associated and distinguished by their much greater solubility in water, and affinity for it; by their solubility in alkohol; by their greater fusibility and volatility, and in general by their greater activity as chemical agents.

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CHAP. I.

## OF AMMONIA AND ITS BASE.

THIS alkali, obtained by indirect processes, was known to the older chemists only in its combination with water, forming the liquid which, from its volatility compared with the other alkalis, was denominated Volatile Alkali. Dr Priestley first shewed, that a permanently elastic fluid can be procured from this by a moderate heat, and that the alkali is gaseous when in its pure form.

In the progress of pneumatic chemistry, several facts were observed, proving the composition of ammonia. Priestley found, that on taking the electric spark in the gas, or on transmitting it through an ignited earthen tube, the volume is much enlarged, and its properties are changed; it is no longer absorbed by water, and is highly inflammable. By heating certain metallic oxides in the ammoniacal gas, he farther found, that they are reduced to the metallic state; a little water appeared to be produced, and the residual gas is nitrogen. Scheele, too, observed the decomposition of ammonia, and the production of nitrogen, particularly in the detonation of fulminating gold, a substance composed of ammonia and oxide of gold.

Berthollet, reviewing and comparing these experiments, was led by them to institute others, in which ammonia was decomposed; and, from the whole, he first inferred that it is a compound of hydrogen and nitrogen gas. In its de-

composition by heat it is resolved into these two gases ; and when decomposed by metallic oxides, the oxygen of the latter combines with the hydrogen forming water, and the nitrogen is evolved.

The composition of ammonia is not easily established by synthesis, the elasticity of the two gases being an obstacle to the exertion of the affinity of their gravitating matter, so that when mixed together they cannot be combined, even by the agency of the electric spark. It had been observed, however, that in some cases of chemical action, ammonia is evidently formed, or is evolved, though it does not pre-exist in the materials. This production of it was known to take place in the action of nitric acid on tin ; and the theory of its production, as well as the principle on which it depends, were ascertained by Dr Austin. Tin being a metal having a great avidity to oxygen, it decomposes when acted on by nitric acid, both the acid itself and the water the acid contains, attracting the oxygen of both. The acid is a compound of oxygen and nitrogen ; when it suffers this decomposition its nitrogen and the hydrogen of the water are evolved : and being presented to each other in the moment of their evolution, and before they have become elastic, (in their *nascent state*, as it has been named), their mutual affinity is exerted with effect, and they combine. Dr Austin farther found, that it was sufficient to present hydrogen in its nascent state to nitrogen gas to form ammonia; this result being obtained when iron-filings moistened with water are confined in a tube with nitrogen gas over quicksilver.

The discovery of the existence of oxygen, as a constituent principle of the other two alkalis, potash and soda, suggested the conjecture, that it might exist as an element

in the composition of ammonia. Mr Davy stated several experiments by which this appeared to be proved, and from which he inferred, that the proportion of oxygen in the composition of ammonia cannot be estimated at less than seven or eight parts in the hundred, and may even be larger. But the reverse was afterwards established by the experiments of other chemists. Dr Henry, submitting ammonia to analysis by the action of electricity, found, when the due precautions have been observed to exclude moisture, that it is resolved into hydrogen and nitrogen alone, without any trace of oxygen. And Berthollet junior obtained the same results, in experiments made with the view of discovering if oxygen were present. If the analogical inference, that ammonia must contain oxygen, from the fact that all other bases which neutralize acids contain that element, be sufficiently strong to warrant such a conclusion, it must be inferred, that oxygen exists either in hydrogen or nitrogen, and under this point of view ammonia may be an oxide with a compound base. But the present state of our knowledge, on this subject, does not admit of any certain conclusion.

The analogy in chemical constitution between ammonia and the other alkalis, appeared to be established under another point of view, by the indication which some experiments afford of its containing a base of a metallic nature. Ammonia itself is not easily subjected to the action of galvanism, but a very ingenious form of experiment was employed by Seebeck, that of placing it in the galvanic circuit in contact with quicksilver. A globule of quicksilver was placed in a solid piece of carbonate or muriate of ammonia, slightly moistened, in connection with the positive side of a galvanic battery, or, according to the

method of Berzelius and Pontin, it may be placed in contact with a solution of pure ammonia in a platina spoon. On establishing the contact with a wire from the negative side, the quicksilver soon begins to increase in volume; it thickens and becomes less mobile, and at length is enlarged to four or five times its original volume, and becomes a soft solid, retaining the metallic lustre: oxygen is, at the same time, evolved at the positive wire. The changes the quicksilver thus suffer are perfectly similar to what would be produced from the communication to it of metallic matter. Hence it was concluded, that in the experiment the ammonia suffers decomposition, probably by the abstraction of oxygen, and that its supposed metallic base, (Ammonium as it was named), remains in combination with the quicksilver. This appeared to be confirmed by the fact, that when potassium, a substance powerful in attracting oxygen, is made to act on ammonia in contact with quicksilver, similar changes are produced; and farther, that when the ammoniacal amalgam, as this soft solid has been named, is dropt into water, it is resolved into quicksilver and ammonia, hydrogen gas being at the same time evolved, which was supposed to indicate a decomposition of water, and the transfer of its oxygen to the ammonium, so as to reproduce ammonia. It was also affirmed to absorb oxygen from the air.

The theory of this singular experiment, however, is far from being elucidated, and some of these statements appear to be incorrect. Gay-Lussac and Thenard consider the soft metallic solid as a compound of quicksilver with portions of ammonia and hydrogen. In its production, according to this view, the water with which the ammoniacal salt is moistened, and the presence of which is abso-



lutely essential to the success of the experiment, is decomposed : its oxygen is attracted to the positive galvanic pole, (or combines with the potassium when it is employed to produce the effect,) while the hydrogen of the decomposed water, and a portion of the ammonia attracted to the negative side, enter into weak combination with the quicksilver, dilating it, and diminishing its specific gravity. And they affirm, what appears to establish this view, that the ammoniacal amalgam, by exposure to heat, or by mere agitation when it is removed from the galvanic influence, is resolved into quicksilver ammonia and hydrogen, without any absorption of oxygen from the air; or when diffused in warm and dry quicksilver, it yields ammonia and hydrogen, without oxygen being communicated to it from any source. Those, again, who maintain the opposite opinion, suppose in these cases the presence of a minute quantity of moisture, to which they ascribe the effect. The proofs given, however, by Gay-Lussac and Thenard, that this is not the case, appear to be just; and the theory which they give of the nature of this substance is confirmed by its analogy to the metallic substances obtained from the fixed alkalis, which, as is afterwards to be stated, probably consist of metals combined with hydrogen. Yet the actual determination of the results by experiment is so difficult, that some uncertainty remains attached to it. Whatever be the ultimate nature of ammonia, however, it is resolvable by any analysis, the whole results of which are obvious and distinct, into hydrogen and nitrogen alone.

The proportions of these originally assigned by Berthollet were 72.5 measures of hydrogen, and 27.5 of nitrogen; others have been assigned not very different. The younger Berthollet states them at 75.5, with 24.5; these are very nearly the proportions of three measures to one

measure, and are conformable therefore to the law, for which there appears to be some foundation, that gases combine in simple proportions estimated by volume. Converting them into weight, ammonia will consist of 81.5 of nitrogen and 18.5 of hydrogen. The condensation attending the combination is equal to half the volume of the whole gases, or twice the volume of the nitrogen; and hence, when ammoniacal gas is decomposed by the electric spark, and converted into hydrogen and nitrogen gases, it is doubled in volume.

Ammonia is always procured by indirect processes. Its ultimate source is usually from the decomposition of animal matter, of which its constituent principles are elements, and which, in the new combinations taking place in that decomposition, unite so as to form it. It is thus obtained abundantly in the distillation of bones and other animal substances. Procured in this way, however, it is always impure, and the chemist therefore usually avails himself of a salt containing it, prepared on a large scale for different purposes in the arts, the muriate of ammonia, or sal-ammoniac of commerce, from which it is easily obtained pure. This salt consists of muriatic acid, combined with ammonia. On mixing it with two parts of slaked lime, the pungent smell of ammonia is immediately apparent; and on applying heat to the mixture in a retort, there is an abundant production of elastic fluid, consisting of the ammonia in this form, the lime combining with the muriatic acid of the compound salt, and the ammonia being disengaged. The ammoniacal gas is received over quicksilver, as it is instantly absorbed by water.

Ammonia, in the state of gas, has an odour extremely pungent, and is so acrid as to inflame the skin. It is one

of the rarest of the elastic fluids; its specific gravity is 0.590, atmospheric air being 1000.—100 cubic inches weigh 18 grains. It is permanently elastic at natural temperatures, but when exposed to a cold  $-56^{\circ}$  of Fahrenheit, it condenses into the liquid state, a condensation facilitated probably by the operation of a minute portion of water which it may hold dissolved. The gas extinguishes combustion; it is itself slightly inflammable, the flame of a taper partially introduced into it being enlarged, and when it is previously mingled with atmospheric air it burns with a slight lambent flame; when kindled in mixture with oxygen gas it burns more strongly; and with detonation on the introduction of the electric spark, when the proportions are within 3 of oxygen to 1 of ammonia, or 3 of ammonia to 1.4 of oxygen. The oxygen combines with the hydrogen of the ammonia forming water, and the nitrogen is evolved; or, if there be an excess of oxygen, part of the nitrogen combines with it, and forms nitric acid. When the ammoniacal gas is kindled issuing from a small tube, and introduced into oxygen gas, it burns slowly.

Ammoniacal gas is largely and rapidly absorbed by water; the water, under a mean atmospheric pressure and temperature, taking up rather more than one-third its weight of the gas. Ice immediately liquefies in it, at the same time condenses it, and this is accompanied by the production of cold. Its solution in water is of inferior specific gravity to pure water, being, when concentrated, not more than 9054. The gas is expelled from it by an elevation of temperature; by intense cold the solution is congealed without the ammonia being separated; the congelation takes place at  $-40^{\circ}$ : and at  $58^{\circ}$  it loses all smell.

It is under the form of the watery solution that ammo-

nia is usually employed as a chemical agent. The solution is prepared by connecting a retort of green glass with the mixture of muriate of lime and ammonia in the proportions already stated, and with about twice their weight of water, with the bottles of Woolfe's apparatus containing water. Heat is applied to the retort by the medium of a sand-bath: the lime combines with the muriatic acid, the ammonia is expelled, and is condensed partly by the water that distils over from the retort, and partly by the water in the bottles of the apparatus through which it is transmitted. On a large scale, the distillation is carried on from an iron-still containing the muriate of ammonia and lime dry, to which the fire is directly applied, the still being connected with a spiral tin tube placed in a refrigerator, and with the extremity of which a series of globular receivers is likewise connected. When properly prepared the solution is colourless, and has the pungency of the ammonia unaccompanied with any foetor.

Ammonia has been supposed to be inferior to the other two alkalis in alkaline power, as they decompose the compounds it forms with the acids. This, however, is probably owing to its volatility: and as a given weight of it neutralizes larger quantities of the acids than the same weight of the other alkalis do, it follows, from Berthollet's views of the strength of chemical affinity, that it is even superior in power. From the inferior concentration, however, of its solution, it acts less strongly on a number of substances; it combines rather less intimately with the oils, and it does not dissolve the earths.

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## CHAP. II.

### OF POTASH AND ITS BASE.

**T**HIS alkali has long been employed in a state of greater or less purity as a chemical agent, and has been distinguished by various appellations. Being usually procured from the combustion of vegetables, it received the name of Vegetable Alkali. As it is the base of the impure alkaline salt, the potash of commerce, it has been named Potash. The term Potassa has been received as the Latin appellation, and would be preferable also in our language, as similar in termination to the names of the other alkalis, and as different from the term applied in commerce to a substance containing only the alkali in an impure form: but that of Potash appears to be established by general use.

Potash had sometimes been suspected to be a compound substance, but these conjectures rested only on remote analogies, and nothing was truly known with regard to its composition previous to Mr Davy's discovery of it. By submitting it to the action of galvanic electricity in high intensity, he decomposed it, and obtained from it a metallic like substance before unknown, possessed of very singular properties, and which has led to the discovery of others equally peculiar.

This experiment is performed by placing a small piece of potash slightly moistened, in a platina cup, in connec-

tion with one extremity of a galvanic battery. On establishing the communication with the other extremity by a platina wire, an effervescence is excited at the surface of the potash at the positive side, owing to the disengagement of elastic fluid; this is accompanied with the liquefaction of the potash; and at the surface in communication with the negative side, there is no sensible disengagement of gas, but globules appear having metallic lustre, and in mobility similar to quicksilver. The elastic fluid disengaged, Mr Davy found, is oxygen gas. In conformity, therefore, to the usual law which regulates galvanic decomposition, it was to be inferred, that the potash had been decomposed, that the oxygen attracted to the positive side is one of its elements; and that the metallic matter appearing at the other side is the base with which the oxygen had been combined.

These conclusions appeared to be established also by synthesis. On exposing the metallic-like matter to atmospheric air, its lustre is diminished, a white crust soon forms upon it, which is potash, and this is accompanied with an absorption of oxygen. On heating it in oxygen gas it enters into vivid combustion; solid potash is produced, and a portion of the oxygen is consumed. Or, on dropping it into water, an immediate disengagement of hydrogen takes place, the metallic matter disappears, and a solution of potash is obtained. From all these experiments, the conclusion appeared to follow, that potash is a compound of this metallic matter and oxygen, since it is resolved into them, and is re-produced when they combine.

A confirmation of this discovery, important, as excluding any suspicion that might have been entertained that

galvanic action is essential to these changes, was soon after made by the French chemists, Gay-Lussac and Thenard, potash having been decomposed by them by the action of iron. Clean iron-filings are put into an iron tube, bent so that the filings shall lie in the curvature towards the middle of the tube. To one extremity of it is adapted, by grinding, a smaller tube having a stopper inserted at its open extremity, and containing a quantity of pure potash; the curved tube is placed across a small furnace, so that the iron-filings are raised to a white heat; the potash is then liquefied by applying to it the heat required, and is allowed to run through a small aperture on the filings. It is decomposed, the iron attracts its oxygen, and the metallic matter, which is its base, is sublimed to the other extremity of the tube, which is kept cold by a freezing mixture. A little hydrogen gas is disengaged during the process, apparently derived from the water contained in the potash, and is allowed to escape by a tube of safety connected with the tube. The metallic matter adheres in brilliant plates to the sides of the extremity of the large tube; it is similar to that obtained from the decomposition of the alkali by galvanism, or at least is only a little heavier. Potash has also been decomposed by charcoal, but the process is not so easily conducted as that with iron.

To the metallic substance obtained in these experiments, the base of potash, Mr Davy gave the name of POTASSIUM. In its general properties it resembles a metal, yet it as well as the other alkaline bases that have been procured, differ remarkably from the common metals in their inferior density, as well as in some other qualities. To distinguish them the term Metalloid has been employed.

Gay-Lussac and Thenard proposed a different view of

these experiments, and of the nature of the substance they afford. They supposed the water present to be decomposed; its oxygen to be evolved at the positive wire, or in the experiment with iron to combine with the iron, and its hydrogen to unite with the potash and form the Potassium. When this substance is submitted to oxygenation, its hydrogen is supposed, in conformity to this view, to combine with the oxygen consumed, forming water, and the potash appears in its original state. And although the Potassium may be produced without the presence of any sensible humidity, this does not invalidate this hypothesis, since even fused potash in its driest state contains a considerable quantity of combined water which will be decomposed.

It followed, however, from this view, that potassium ought by oxygenation to form an alkali, containing combined water similar to fused potash, while if potassium be the base of potash forming it by oxygenation, the product of this oxygenation must be the real alkali free from water. From experimental researches on this point, it appears, that the product of the oxygenation of potassium does not contain water, or at least does not contain such a quantity of water as is contained in fused potash. The hypothesis of Gay-Lussac and Thenard, therefore, cannot be maintained, and they have accordingly relinquished it.

Another view of this subject, however, may still be proposed, and seems indeed to be indicated by the phenomena connected with the production of potassium. When potash is submitted to galvanic action, an effervescence is perceived at the positive galvanic wire from the evolution of oxygen gas, but there is no disengagement of gas at the negative wire, there is merely the production of the globules of potassium. These are the phenomena that



ought to appear on the hypothesis that potash is an oxide of potassium, and that fused potash is the real alkali. But fused potash is not so; it contains at least 0.20 of combined water: when submitted to galvanic action, this water must suffer decomposition; its oxygen will, in conformity to the usual law, be given out at the positive side; its hydrogen will be given out at the negative side; and being twice the volume of the oxygen, its evolution ought to be equally apparent. Since it does not appear, it may be inferred that it enters into the composition of the metallic matter, which appears at the negative side. The hypothesis, however, that the metallic product is a compound of potash and hydrogen, cannot be maintained. But there is another mode in which the results may be explained. Potash may be regarded as a compound of a metallic base with oxygen, and, as decomposed by galvanic action, its oxygen being attracted to the positive, its base to the negative pole. But the combined water which always exists in the fused potash must also be decomposed in this experiment: its oxygen will be disengaged at the positive side, while its hydrogen, attracted to the negative side, may combine with the real metallic base, and the potassium may be the product of this combination,—not a real metal, but a metallic hydru-ret, or compound of a metal with hydrogen. The experimental evidence by which this conclusion is to be established, is to determine whether potassium by oxygenation forms a product equal or inferior in alkaline strength to the real alkali, ascertaining the strength of the latter by making due allowance for the quantity of combined water which fused potash contains. The result of the experiments I have made on this subject, is, that the potash formed by the oxygenation of potassium, though superior in al-

kaline strength to fused potash, is not equal to real potash; it must therefore contain a portion of combined water, and hence potassium probably must contain a proportion of hydrogen united with the real metallic base. This view of the constitution of this substance accounts for its peculiar qualities, and particularly for its great levity, a quality in which it differs so remarkably from metals, and which may be supposed to arise from the presence of hydrogen. A similar view may be extended to the other metallic products from the alkalis and earths, and even some of the common metals, it is possible, may contain hydrogen.

It remains to state the properties of POTASSIUM. It appears in the form of globules, having metallic lustre and opacity at the temperature of 60, similar in appearance to those of quicksilver, but less mobile. At 70° the mobility and fluidity are greater, and at 100 or 136° it is completely liquid, so that the globules run easily together. At 50 it becomes solid, is similar in appearance to silver, and is malleable; at 32 it is hard and brittle. Though it resembles the metals in opacity, lustre, and other properties, it differs from them remarkably in density: in this property it is inferior even to water or alcohol: when liquid it does not sink in naphtha, the specific gravity of which is 0.77: in its solid state it is rather heavier, but still even at 40 it floats in this liquid; its specific gravity, therefore, is not more than 0.6, water being 1; according to Gay-Lussac, however, it is 0.86.

Potassium, though so remarkably affected by heat, is not very volatile; it requires a temperature approaching to ignition to volatilize it. At temperatures inferior to this it combines with oxygen slowly, and without any sensible

combustion; but when heated to the point of volatilization, it burns vividly with intense heat and light.

Potassium combines with different proportions of oxygen. The product of its combustion is a solid white mass, which Sir H. Davy inferred is potash, and in the formation of which he concluded that about 18 of oxygen are combined with 100 of potassium. When it is more gently heated in oxygen gas, so as not to inflame, a solid of a greyish colour is formed, which he considered as consisting partly of potash, and partly of potassium, in a low degree of oxidation. Very different results, with regard to this, have been established by Gay-Lussac and Thenard: The substance formed by the combustion of potassium they find is not potash, but a product at a higher degree of oxidation, containing three times the quantity of oxygen which potash contains; it is of a yellow colour, and is fusible; when water is added to it there is an effervescence from the disengagement of oxygen, and it is converted into potash; it also yields oxygen to inflammable bodies. The degree of oxidation of potassium which forms potash, appears to be established almost exclusively by the agency of water; the proportion of oxygen with which the potassium combines, is about 20 with 100 parts; hence potash consists of 83.37 of potassium, and 16.63 of oxygen. There is lastly a product obtained from the oxygenation of potassium, by inclosing it for some days in a small vessel loosely covered, which is dull, brittle, and inflammable, and which Gay-Lussac and Thenard regard as an oxide in the first degree of oxidation.

From its strong attraction to oxygen, potassium decomposes water with rapidity, producing explosion with flame, and being converted by oxygenation into potash. Placed

on ice it burns with a bright flame melting the ice. It attracts oxygen with similar rapidity from the mineral acids, and burns; and also from various oxidated substances. It thus changes the constitution of the other alkalis and alkaline earths. Its action on ammonia is singular. When heated in it, the ammonia disappears, hydrogen gas in a similar volume is produced, and an olive coloured substance is formed, the nature of which is not yet well ascertained.

Potassium unites with inflammable substances. When heated in hydrogen gas, it diminishes in volume: and the gas, on being mingled with atmospheric air, explodes with the production of alkaline fumes. If a more gentle heat be applied, a solid compound containing a smaller proportion of hydrogen is formed, which is of a grey colour, without metallic lustre, and inflammable. With phosphorus, a compound is formed, inflammable, and which has the appearance of the metallic phosphurets. When heated with sulphur, under the vapour of naphtha, they combine rapidly with the evolution of heat and light, and form a substance of a grey colour, with the lustre and appearance of artificial sulphuret of iron.

It also combines with the metals, and forms compounds having metallic properties, which absorb oxygen from the air and decompose water, potash being formed, and the metal separated unchanged. Its action on quicksilver is singular. They instantly combine with the evolution of more or less heat: the potassium in a minute quantity adds to the consistence of the quicksilver, and diminishes its mobility: when the quantity is about  $\frac{1}{10}$  of the weight of the quicksilver, the amalgam is soft and malleable: in a quantity a little larger it renders it solid, and nearly simi-

lar to silver in colour. When it amounts to about  $\frac{1}{10}$  of the weight of the quicksilver, the alloy is hard and brittle. The fluid amalgam dissolves all the metals, even those with which quicksilver alone does not combine. Compounds of the metals with potassium are likewise formed by heating an excess of it with the metallic oxides, one portion of it abstracting oxygen and forming potash, the other uniting with the reduced metal. From this action it acts on glass, reducing the oxides of iron and lead which it contains, and forming potash, which dissolves the glass.

After this account of the properties of potassium, it remains to give the chemical history of POTASH.

Potash is usually procured from the combustion of land vegetables, the process being carried on in those countries which abound in wood. The ashes remaining after the combustion being lixiviated, the liquor affords on evaporation, saline matter, which, when exposed to heat, forms a solid white mass. This consists of various salts, principally of potash, combined with carbonic acid, partly also of potash combined with sulphuric and muriatic acids, together with siliceous earth, oxides of iron and manganese, and occasionally other impurities. The alkaline matter is obtained in different quantities from different vegetables: the harder woods afford more than those that are spongy, shrubs more than trees, herbaceous plants a quantity still larger, and even different parts of the same plant give different proportions of it; the leaves, from a given weight, yielding more than the branches, and the branches more than the trunk.

Potash is sometimes procured from other sources, and in a state more pure, as from the decomposition by heat of

the salt named Tartar, or the deflagration of nitre with charcoal, this alkali being the base of these salts.

Potash, as obtained by all these processes, is combined with carbonic acid. To abstract this, the saline matter, the Sub-Carbonate of Potash as it is named, is first freed from the other ingredients by lixiviation, and evaporation of its solution, and is then mixed with twice its weight of recently slaked lime, and as much water as is necessary to give the consistence of a thin paste: this is put into a glass funnel, the tube of which is obstructed with a piece of linen; the mass of lime soon subsides, so that the liquid portion filtrates through it slowly, and water is occasionally added, as the filtration proceeds, until a quantity of liquid has passed through ten times the weight of the sub-carbonate of potash employed. The lime in this process attracts the carbonic acid, and, from the large quantity employed, and the slowness with which the water holding the alkali dissolved passes through it, the abstraction is more complete than could be obtained by any other arrangement.

Still, though the potash is thus obtained in a state of solution nearly pure, it is not perfectly so; a little carbonic acid remains combined with it, and there may also be present small portions of sulphate and muriate of potash, and siliceous earth. To obtain it in a state of purity, different methods have been proposed; that which is generally followed is one proposed by Berthollet. Potash is soluble in alcohol, but is insoluble when combined with carbonic or sulphuric acid. The alkaline solution, therefore, obtained by slow filtration from the mixture of sub-carbonate of potash and lime, is evaporated until it become of a thick consistence, and there is then added to it an equal weight of alcohol. A quantity of undissolved matter subsides, a

dark-coloured liquid floats above this, which is principally water holding dissolved potash combined with carbonic acid; a lighter coloured liquor is above this; it is drawn off, and is partially evaporated in a silver bason. On standing, it separates into two liquids of different specific gravities, the heavier being a solution of the alkali with carbonic acid, the lighter a solution of the pure alkali. The latter is poured off, and is evaporated, so that on cooling it shall either deposit crystals, or pass into an irregular crystallized mass; a small portion of residual liquor being poured off, the potash is thus obtained in a solid form.

Potash thus prepared is obtained by evaporation in a solid mass, hard, and brittle, of a greyish white colour. If evaporated to a less extent, it crystallizes in forms which are modified by the degree of evaporation: it is thus obtained in thin plates, in slender needles, or in tetrahedral pyramids, single or double, these containing different portions of water of crystallization. They produce cold in dissolving in water, while the solid potash produces heat. Even in the driest form to which it is reduced by evaporation, and after it has been kept in fusion, the potash retains a considerable quantity of water combined with it, and which cannot be abstracted from it, as by applying heat to expel it, the potash itself is at length volatilized, and its combined water is separated only when it enters into combinations. The quantity has been variously estimated. D'Arcet, by whom the fact appears to have been first observed, stated it at 0.27, Berthollet stated it at 0.14, Berard at 0.20, and with this last estimate that by Davy and Gay-Lussac nearly corresponds. The potash in this state, as well as in its crystallized forms, is a Hydrate: in the latter the proportions of water are larger. The combined water

gives rise to a considerable modification of properties. The real alkali obtained by the combustion of potassium, and heating the product to expel the excess of oxygen, is of a greyish colour, harder and heavier than fused potash, with a vitreous fracture; it requires a strong red heat to melt it, and a higher heat to volatilize it. When a little water is added to it, it becomes white and more fusible and volatile. This hydrate melts at a heat of  $360^{\circ}$ , and is volatilized at a low red heat. It still has a strong attraction to an additional portion of water: it imbibes it rapidly from the atmosphere, so that its surface becomes humid, and it dissolves in less than its own weight of water, forming a solution dense and somewhat viscid.

Potash has the distinguishing alkaline property, that of combining with acids, and neutralizing the acid powers, though, as a larger quantity of it is necessary to saturate a given weight of acid than is required of ammonia or soda, it is perhaps inferior to them in real alkaline power. Its alkaline strength, however, is very considerable: a minute portion of it changes the blue and purple colours of vegetables to a green, and it is so powerfully corrosive as quickly to erode and dissolve animal matter.

It unites with oils and fats, forming soaps, which though concrete, are soft or gelatinous.

With some of the earths it combines by fusion, and others it dissolves even in the state of its watery solution.

It has little energy of action on the metals, but combines with some of their oxides. It unites too with sulphur and phosphorus, rendering them to a certain extent soluble in water, and enabling them to decompose it by attracting oxygen.

According to Gay-Lussac and Thenard, it combines



with an additional portion of oxygen, by exposing it to the air for a short time at a red heat. This excess of oxygen is expelled by the action of water.

From the numerous and powerful chemical actions which potash exerts, it is applied to many purposes of utility in the arts, and as it is the alkali most easily procured, it is the one most extensively used. It is thus employed in bleaching, dyeing, soap-making, the manufacture of glass and others. In medicine it is employed as an antacid, a lithontriptic, and an escharotic.

Besides being produced in the vegetable, it is found in the mineral kingdom, either as a saline combination, or as an ingredient in some earthy fossils. It also exists in several of the animal fluids and solids.

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### CHAP. III.

#### OF SODA.

**SODA** being found more extensively diffused in the mineral kingdom than either of the other alkalis, has been denominated Mineral Alkali. The term Soda is that usually applied to it, and is unexceptionable.

On the discovery of the composition of potash, Sir H. Davy submitted soda to the same method of analysis, and discovered, that it affords a base of a similar nature. It required for its decomposition rather a greater degree of galvanic power than potash did ; but when this was applied in sufficient intensity, the phenomena were similar ; an effervescence was produced at the positive side, which was found to arise from the disengagement of oxygen gas ; and at the surface in contact with the negative wire, globules were produced having metallic lustre. This matter, exposed to the air, absorbed oxygen, and reproduced soda ; the same result took place more speedily, and with the phenomena of combustion, when it was heated in oxygen gas, or when dropt into water, a solution of soda was formed, with an extrication of hydrogen gas. These experiments seemed to lead to a similar conclusion as that drawn with regard to potash,—that the soda placed under galvanic action suffers decomposition, that the oxygen disengaged at the positive pole is derived from this, and that the metallic matter collected at the negative side, Sodium, as it is named, is the base with which the oxygen had been

combined. The same theory is probably to be adopted with regard to this as with regard to potassium. The strict analogy between them leads to the conclusion, that if the latter contain hydrogen combined with a metallic base, the former is of similar constitution ; and as soda contains combined water as well as potash, the same changes may occur in its galvanic decomposition.

The process of Gay-Lussac and Thenard of decomposing the alkali by iron, does not succeed so easily with soda as with potash : the easiest process for obtaining sodium, is to decompose soda, by heating ignited muriate of soda by potassium.

The following are the properties of SODIUM : It is white and opaque, with metallic lustre, having the general appearance of silver ; it is very malleable, and is so soft, that with a slight force it can be extended in thin leaves, a softness which it retains even when cooled to  $32^{\circ}$ . Though lighter than water, its density is considerably greater than that of potassium : Mr Davy estimates its specific gravity at .9348, Gay-Lussac at .97223. It requires a higher heat to melt it than potassium does : at 120 it begins to lose its cohesion ; at 180 it is fused : it is also less volatile, as it remains fixed even at ignition.

When exposed to the atmosphere it is oxidated, soda being formed on its surface, which deliquesces slowly. When heated nearly to ignition in atmospheric air, the combination is attended with combustion ; and when heated in oxygen gas, it burns with a vivid white light, emitting bright sparks. Like potassium it combines with oxygen in different proportions. The product of its combustion is an oxide containing one half more oxygen than soda ; it is a substance of a dull greenish colour, fusible, and loses this excess of oxygen by the action of water. The propor-

tions in soda are 74.5 of sodium, and 25.5 of oxygen. The existence of an oxide at a lower degree of oxidation is stated by Gay-Lussac : it is of a greyish colour, dull and brittle, and is obtained by the same process as the protoxide of potassium.

From its strong attraction to oxygen, sodium decomposes water rapidly, soda being formed by its oxygenation, and hydrogen disengaged ; and if the water is in small quantity, the heat produced is such as to inflame the sodium. It is inflamed too by nitric acid, and is rapidly oxidated by the other acids. It also attracts oxygen from metallic oxides, and exerts an action on ammonia similar to potassium.

Sodium does not appear to be dissolved when heated in hydrogen gas, but at a high degree of heat a combination between them is established, the gas burning when it escapes into the air. It combines with sulphur and phosphorus, the combination being attended with the evolution of much heat and light, and the compounds being similar in external properties to those formed by potassium with the same inflammables.

It unites too with the metals, forming compounds which retain the general metallic properties. When combined with quicksilver in so small a proportion as  $\frac{1}{10}$ , it renders it fixed, forming a solid which has the appearance of silver. All these compounds are decomposed by exposure to air or water, the sodium by absorption of oxygen being converted into soda. With potassium it unites in various proportions forming alloys, in general more fusible than either.

SODA is usually obtained from the combustion of marine vegetables, of which different species afford it in different

quantities and states of purity. The various kinds of fuci or sea-weed afford in this country the impure alkaline product, known by the name of Kelp ; on the shores of the Mediterranean, the *salsola*, *salicornia*, and others, afford the purer *barilla*. Even, it, contains much foreign matter : the soda is combined with carbonic acid, and with this are associated muriate and sulphate of soda, charcoal, lime, magnesia, and siliceous and argillaceous earths. The origin of the soda afforded by the process is not altogether determined, but it is most probable that it is ultimately derived from the muriate of soda with which these plants are from their situation supplied ; as when they are transplanted to an inland situation, it is established by the experiments of Du Hamel and Cadet, that the quantity they afford diminishes progressively, and after some years they afford only potash. Vauquelin's experiments prove, that in the *salsola* soda, carbonate as well as muriate of soda exists previous to the combustion.

It is usually from *barilla* that soda is procured. The *barilla* in powder being lixiviated with boiling water, the solution on evaporation affords crystals of the salt formed by soda with carbonic acid. To obtain the soda from this, it is dissolved in twice its weight of water, to which is added as much lime newly slaked as gives a thick consistence : this being poured into a glass funnel, in the neck of which a piece of linen is put, water is added as the filtration proceeds slowly, until the quantity of solution is equal to five or six times the weight of the sub-carbonate that had been employed. The lime abstracts the carbonic acid, its affinity to it being aided by the large quantity of it used, and the slowness with which the solution passes through it. Still the soda has a small quantity of carbonic acid combined with it : to obtain it pure, therefore, it re-

quires to be submitted to the action of alkohol, in the manner described under the history of potash : though the process scarcely succeeds so well.

Soda thus obtained is in the state of a solid white mass, which is crystallized with difficulty ; its crystals are prisms, but are not regular : even in its driest state, it contains, like potash, a portion of combined water ; which cannot be expelled by heat : the quantity has been estimated at 0.18.8, at 0.20, and at 0.25. This water modifies its properties, the alkali obtained by the oxidation of sodium being of a grey colour, harder, heavier and less fusible than the hydrate. The latter melts at a red heat, and at a higher heat is volatilized. When exposed at a red heat to the air, it combines according to Gay-Lussac with a portion of oxygen, and passes to the oxide at the maximum of oxidation.

Soda has all the alkaline properties equally with potash. It is acrid and caustic, and abundantly soluble in water. It changes the vegetable colours to a green, and combines with the acids, neutralizing the acid properties : with oils it forms soap ; with siliceous earth it unites by fusion and forms glass : it combines too with sulphur and phosphorus, rendering them soluble in water, and enabling them to decompose it.

So close is the resemblance in properties between these two alkalis, that the distinctions between them require rather minute attention to discover them. Soda appears to have a less strong attraction to water ; in their combinations they can be at once distinguished, the salts formed by the one united with the acids, having qualities altogether different from those of the other. Both are applied to the same purposes.

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BOOK IV.

## OF EARTHS AND THEIR BASES.

THE earthy aggregates which occur in nature are usually heterogeneous or compound; but by analysing them, chemists have arrived at the knowledge of a few substances, of no lustre or transparency, having a loose texture, insoluble in water, or sparingly soluble, unflammable, difficultly fusible, and of moderate specific gravity. These resisting farther analysis, they regarded as simple substances, distinguishing them by the name of Earths, and thus affixing to this term a signification different from that which it has in popular or even in mineralogical language. Four substances of this kind were known to the older chemists, *silex*, *argil*, *magnesia*, and *lime*: *barytes* and *strontites* were afterwards made known, and more lately, *zircon*, *glucine*, and *ittria* have been added to the number.

The important discovery has also been made, that they are not simple substances but compounds, their bases being somewhat similar to those of the alkalis, and these bases being united with oxygen. From the similarity of the earths to metallic oxides, they had often been supposed to be of a metallic nature, and their reduction had frequently been attempted, and at one time had even been supposed to have been accomplished. This, however, was a mistaken result, and nothing was known with regard to their composition, until Mr Davy, after his disco-

very of the chemical constitution of the alkalis, submitted the earths to the action of galvanism. Though results were obtained indicating their composition, these were less perfect than those obtained with regard to the alkalis, owing partly to the strength of affinity between their principles, partly to their being less perfect electrical conductors. By submitting them to the galvanic action in mixture with potash, or with metallic oxides, results more distinct were obtained: and a method employed by Berzelius and Pontin proved still more successful,—placing them in the galvanic circuit with quicksilver. They thus obtained the metallic bases of barytes and lime in combination with the quicksilver. Mr Davy, by the same method, decomposed strontites and magnesia. By submitting silex, argil, zircon, and glucine, to the action of the galvanic battery in fusion with potash or soda, or in contact with iron, or by fusing them with potassium and iron, appearances were obtained indicating their decomposition, and the production of bases of a metallic nature: and there can remain little doubt, that all the earths are compounds, and of similar constitution.

The metallic bases of the earths approach more nearly than those of the alkalis to the common metals, and the earths themselves have a stricter resemblance than the alkalis to metallic oxides. Yet there are also grounds for retaining their distinction as a natural order, forming the link which connects the alkalis with the metals.

Of the characters assigned to the earths, none can be regarded as altogether distinctive. They are usually said to be insipid; but there are three of them, barytes, strontites, and lime, which have a strong taste: they have also been considered as insoluble in water; but these earths are



soluble to a certain extent. Infusibility is a character less equivocal, as there is none of them but what requires a very intense heat for its fusion. They are altogether un-inflammable, a property obviously arising from their being substances saturated with oxygen. Barytes, however, absorbs oxygen at a high temperature, a property in which it resembles the fixed alkalis. In common with metallic oxides, they are destitute of metallic lustre and opacity.

The earths combine with the acids and neutralize the acid properties; these combinations, in the laws they observe, and the compounds to which they give rise, being similar to those which the alkalis form with the acids. There is an exception to this in one earth, silex, which, in the humid way, scarcely unites with any acid but the fluoric, and with it does not produce the state of neutralization. It is the substance, therefore, which is at once most remote from the alkalis, and from the metallic oxides.

One property has been assigned as distinctive of the earthy from the metallic salts, that the solutions of the former are not precipitated by prussiate of potash. This is not, however, without exceptions, the earth named ittria, and also, as Klaproth has affirmed, zircon, giving precipitates with this test. In general, the earthy salts are not much altered by infusion of galls, a re-agent which so sensibly affects metallic salts: neither are they coloured. Ittria affords also, however, an exception to this, some of its salts having a red colour, and being precipitated by infusion of galls; and from these circumstances it ought perhaps to be transferred to the class of metals, though it has not been actually reduced to the metallic state.

Several of the earths combine with sulphur and phosphorus, and render them soluble in water.

The earths and alkalis combine. By fusion with either of the fixed alkalis, they form glasses, and the alkali digested with water on several earths, dissolves a portion of them. They combine with the metallic oxides by fusion, forming coloured glasses, and they even exert mutual affinities in the humid way, producing in their mixture moistened with water a degree of induration.

Lastly, the earths exert affinities to each other. Several of them combine by fusion, forming glasses more or less transparent. And when boiled together in water, it frequently happens, that an earth insoluble by itself is dissolved by the affinity exerted to it by another earth, which is itself of sparing solubility. Their mutual affinities exerted in the humid way is well displayed by another fact, that if solutions of two earths in the same solvent be mixed together, they in different cases combine, the power of the solvent is overcome, and they form an insoluble precipitate. And in all these combinations, the earths modify materially the properties of each other.

Of the different earths, barytes, strontites, and lime have properties considerably analogous to those of the alkalis. They are to a certain extent soluble in water; their solution has an acrid taste, and changes the vegetable blue and purple colours to a green. They have hence been named Alkaline Earths, and, as has been already remarked, it has even been proposed to transfer them from the class of Earths to that of Alkalis. They are, on the whole, however, more strictly connected with the other earths; and they may be placed at the head of the order, forming the transition from the alkalis.

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CHAP. I.

## OF BARYTES AND ITS BASE.

THIS earth was discovered by the Swedish Chemists, Scheele and Gahn. It received the name of Terra Pondrosa, from the great weight of some of its combinations, a name changed by Kirwan to Barytes. It occurs in nature combined with sulphuric acid and carbonic acid.

This earth had always been supposed to be of a metallic nature, partly from the great weight of its native combinations, and partly from some of its saline compounds proving poisonous to animals. Mr Davy, on placing it slightly moistened alone, or mixed with potash, in the galvanic circuit, obtained appearances of decomposition, and the evolution of metallic matter. The method discovered by Berzelius and Pontin, of placing the barytes in contact with quicksilver, in communication with the negative side of the galvanic battery, succeeded more completely; the quicksilver had its fluidity diminished, and on exposing it to the air, it became covered with a film of barytes. And the experiment was still more successful in substituting oxide of quicksilver. An amalgam was thus obtained, from which the quicksilver was separated by distillation, leaving the metallic base of the barytes, a substance which Mr Davy named BARIUM, and which, as obtained by this experiment, he found possessed of the following properties.

It is solid, of a white colour, with metallic lustre, having

a resemblance to silver. It melts at a heat inferior to ignition, but is not volatilized even when heated to redness. Exposed to the air, it tarnishes rapidly, and falls into a white powder, which is barytes, oxygen being absorbed. Dropt into water, it immediately decomposes it, evolving hydrogen, and being converted into barytes. It sinks not only in water, but in sulphuric acid, and Mr Davy supposed it to be four or five times heavier than water. It is flattened by pressure strongly applied. He was unable to determine the proportion of oxygen with which it is combined; but he has since supposed, from indirect experiments, that the earth consists of 89.7 of barium, and 10.3 of oxygen. According to Gay-Lussac and Thenard, barytes, when heated in contact with the air or with oxygen gas, absorbs oxygen rapidly; it thus vitrifies at the surface, and becomes of a greyish colour; this excess of oxygen it yields to inflammable bodies: it also parts with it on the contact of water. Barium, therefore, like potassium and sodium, appears to be susceptible of various degrees of oxidation, and the lower oxide forms the alkaline earth.

BARYTES is procured either from the native carbonate or sulphate. From the former it is obtained, as Dr Hope shewed, by urging it with the powerful heat of a forge fire in a black lead crucible, the carbonic acid being expelled; and by dissolving the residual matter in water, the barytes may be crystallized. The sulphate may be decomposed by exposing it to a red heat for two hours in a covered crucible, mixed with one-third its weight of charcoal. By adding water to the residual matter, a compound of barytes with sulphur and sulphuretted hydrogen is dis-

solved; from this the barytes may be precipitated in the state of carbonate, by the addition of carbonate of potash; or by adding nitric acid, nitrate of barytes is formed, and can be obtained crystallized; and either the carbonate or nitrate thus procured can be decomposed by exposure to heat, and the pure earth obtained.

As afforded by these processes, it is in the state of a grey, solid mass; its taste is extremely harsh and caustic. Exposed to the air it splits, falls to pieces, and is at length reduced to a white powder,—changes analogous to the slaking of lime, and arising from absorption of water.

Barytes is always in the state of a hydrate when obtained by the medium of water; but when obtained from the decomposition of the nitrate by heat, it appears to be free, or nearly so, from combined water. It is then in the form of a grey solid mass, having a specific gravity of 4: on exposure to the air, it slakes and falls to powder, gaining weight from the absorption of water; a similar change is produced by the affusion of water. When a sufficient quantity is added, it dissolves, and afterwards consolidates in transparent needle-like crystals as the solution cools. The dry powder, after exposure to a red heat, seems to contain about 0.09 of combined water; the crystals contain a considerably larger quantity. The influence of the affinity of water to barytes, in aiding the decomposition of its salts, has been already noticed, (page 299), and is to be more fully explained. The fusibility of this earth has been variously stated, according as it is combined or not with water. The crystals melt at a very moderate heat, but this is from aqueous fusion, and as the water is dissipated, a dry powder remains, which, by an increase of heat, may be melted into a semi-transparent glass. The

fusibility of this, however, is still owing to the presence of water; for when this is expelled, or when the real barytes, obtained from the decomposition of the nitrate is submitted to experiment, the most intense heat is necessary to produce fusion.

Barytes is soluble in water, but the degree of its solubility has also been variously estimated, according to the quantity of combined water it contains. The crystallized barytes is soluble in 17.5 of water at 60°: in a drier state it requires about 25 parts; boiling water dissolves one half its weight, and the solution affords crystals on cooling. The crystals are described by Dr Hope, who observed the crystallization of this earth, as flat six-sided prisms acuminated by four planes. They lose their water on exposure to the air, and they suffer the same change from the application of heat. The watery solution has a strong acrid taste, and changes the vegetable blue colours to a green; a film forms on it when exposed to the air from absorption of carbonic acid.

Barytes combines with the acids; and as it decomposes a number of the salts which the alkalis form with the acids, it has been supposed to exert to them stronger attractions. These decompositions appear, however, rather to be owing to the exertion of the force of cohesion, from the insolubility of the compounds which it forms with these acids, than to superior strength of affinity: hence it is only with regard to those acids with which it forms insoluble compounds, that this effect is observed; and in the power of neutralizing the acid properties, it is inferior to the alkalis, and to the greater number of the other earths.

Barytes unites by fusion with the fixed alkalis, and like-

wise with several of the earths ; there are others with which it does not combine. It combines with several of them in the humid way, and communicates to them solubility, or otherwise modifies their properties. Thus it renders argil soluble in water, and silex it enables to combine with different acids.

It combines with sulphur, either by fusion or by boiling in water, and by a resulting affinity enables the sulphur to decompose the water. It exerts a similar action on phosphorus. And it unites with several metallic oxides.

A chemical property which has been assigned to barytes, as distinctive of it, is that of its salts giving a precipitate with prussiate of potash, a property not belonging to the other earths, but characteristic of the metals. This precipitation, however, arises from the impurity of the prussiate. When pure, no immediate precipitation is produced by it in the barytic salt, though, after a few hours, if the solution is sufficiently concentrated, crystals of prussiate of barytes are formed.

This earth exerts considerable activity on the living system, and several of its salts prove even poisonous.

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CHAP. III.

## OF STRONTITES.

THE native carbonate of strontites, found at the mine of Strontian in Argyleshire, had been considered as a variety of carbonate of barytes, until Dr Hope shewed that the earth it contains is different from barytes and from any other. He at the same time pointed out its principal properties and chemical relations. Klaproth also and Pelletier afterwards demonstrated the existence of this as a distinct earth. It derives its name from the place where it was first found. It has since been discovered native in different countries in the state of sulphate.

The decomposition of this earth has been effected by submitting it to the action of galvanism, in contact with quicksilver, in the same manner as barytes, and by a similar process its base has been obtained. To this base Mr Davy gave the name of STRONTIUM. Its properties have been only imperfectly examined. In lustre, colour, specific gravity, and other physical properties, it appeared to be similar to the metallic base of barytes; by exposure to the air it is converted into strontites, absorbing oxygen, and gaining weight in this conversion.

STRONTITES is obtained from either the native carbonate or sulphate, by processes the same as those which have been described under the history of barytes. It is in



the state of a dry solid mass having a specific gravity between 3 and 4. By dissolving it in boiling water, and allowing the solution to cool, crystals are formed an inch in length, the form of which is a thin quadrangular table, or compressed prism, sometimes bevelled at the extremities; they are transparent, but become white and opaque on exposure to the air, from losing their water of crystallization. The taste of this earth is less harsh than that of barytes, and it is not poisonous.

Crystallized strontites exposed to heat liquefies from the augmented solvent power of the water of crystallization; when this is expelled, the crystals lose 0.68 of weight, and a dry powder remains, which is probably a hydrate, as a similar powder is produced by the affusion of water on the ignited earth, obtained by the decomposition of the nitrate. This powder cannot be fused even by a very intense heat.

Strontites is soluble in water, the crystals requiring 50 parts at 60°; boiling water dissolves half its weight nearly. In its dry and uncrystallized state, it requires a much larger quantity, nearly 200 parts at 60°. The solution changes the vegetable colours to a green. This earth is likewise soluble in alcohol.

Strontites combines with the acids forming salts, of which some are soluble and crystallizable; others insoluble. The same superiority in strength of affinity has been ascribed to this earth as to barytes, from its decomposing the salts of the alkalis and other earths, but this probably arises from the same cause, the insolubility of the compounds it forms with the acids of the salts in which it occasions these decompositions. Its salts are in general decomposed by barytes. Dissolved in alcohol, they give it

the property of burning with a blood red flame, a property which has been assigned as one of those distinctive of this earth.

Strontites exerts no peculiar action on the alkalis, nor in general on the other earths, though with some of the latter it combines by fusion. It unites with sulphur; the compound is soluble in water, and at the same time decomposes it. On phosphorus its action is similar.

This earth resembles barytes in so many of its properties, that distinctive characters require to be pointed out, by which they may be discriminated. Strontites is less soluble in water; the forms of its crystals are different; its salts, particularly the nitrate and muriate, are considerably more soluble in water, and their solubility is augmented in a greater ratio by heat; they are decomposed by barytes; and they give a blood red colour to the flame of combustible bodies. Two re-agents distinguish them in their combinations. The watery solution of strontites is not like that of barytes precipitated by mallic or gallic acid: and when the salts of strontites are decomposed by oxalic acid, the precipitate is not redissolved by an excess of acid, as that from the barytic salts is; nor, if the solutions are dilute, does the precipitate appear from the barytic salts, while it is sensible from those of strontites.

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### CHAP. III.

#### OF LIME.

**T**HIS earth exists in great abundance in nature, usually in combination with acids. Its compound with carbonic acid forms the numerous varieties of marble, limestone, chalk and marl: with sulphuric acid it forms gypsum or plaster stone; and in these and other saline combinations it exists in the water of springs, in the water of the ocean, in vegetable and in animal matter.

Submitted to the action of galvanism in high intensity, lime in Sir H. Davy's experiments gave indications of decomposition; and when the method described under the history of barytes was employed, he obtained the amalgam of its base. This amalgam exposed to the air or to water, absorbed oxygen, lime being reproduced. In an experiment designed to obtain the base in an insulated state by distilling the quicksilver from it, the tube broke while warm, and at the moment that the air entered, the metal, which had the colour and lustre of silver, took fire, and burnt with an intense white light into quicklime. To this base Mr Davy gave the name of **CALCIUM**.

Lime is obtained with most facility from the native carbonate, from which, by a strong heat, the carbonic acid may be expelled. This process is conducted on a large scale on the different varieties of limestone. As it is not obtain-

ed altogether pure, the chemist, to have it in a state of purity, dissolves marble or chalk in diluted muriatic acid, leaving an excess of lime undissolved : any precipitate afforded by the addition of pure ammonia is separated ; argil or magnesia is thus separated ; the solution is then decomposed by carbonate of potash or soda, and the carbonate of lime being washed with water and dried, is decomposed by heat.

Lime is white, moderately hard and brittle : exposed to the air it quickly absorbs water, which diminishes its cohesion, and causes it to fall down into a white powder extremely fine ; this is the slaking of lime. It takes place rapidly from the effusion of water ; the quantity absorbed is equal to one-fourth of the weight of the lime ; and from its transition to a solid state in combining with the lime, caloric is evolved ; producing considerable heat. This hydrate contains about 0.25 of water.

Lime is infusible ; at least it does not melt in the intense heat excited by the concentration of the solar rays by the most powerful burning mirror, or that excited in the burning of combustible matter by oxygen gas.

It is soluble in water ; it presents the singularity of being less soluble in hot than in cold water : water at  $60^{\circ}$  dissolving  $\frac{1}{11}$  of lime, or  $\frac{1}{14}$  of hydrate of lime ; while at  $212^{\circ}$  it dissolves only  $\frac{1}{12}$  of the former, or  $\frac{1}{15}$  of the latter. The solution, Lime water as it is named, has a strong styptic taste, and changes the vegetable blue and purple colours to a green. Exposed to the air, a film forms on its surface from the absorption of carbonic acid, and the whole of the lime nearly is at length precipitated in the state of carbonate. The same absorption of carbonic acid takes place in dry lime, though much more slowly.

With the acids lime combines, neutralizing the acid properties. Its salts are in general decomposed by potash or soda, either of which precipitates the lime from their solutions; but not by ammonia, probably from the tendency which this alkali has to form a ternary compound with the acid and the lime.

Lime does not combine with the fixed alkalis by fusion, nor with barytes or strontites; but it unites either in the humid way, or by the application of heat, with magnesia, argil and silix.

It combines with sulphur and with phosphorus, rendering them soluble in water, and capable of decomposing it at a low temperature. It melts too, with several of the metallic oxides, forming coloured glasses; it even exerts affinities to several of them in the humid way, and in consequence of these affinities promotes the oxidation of the metals themselves by the action of air or water.

Of the different earths, lime is most extensively used. It is applied as a manure in agriculture; it forms the basis of mortar; the induration of which depends on the gradual intimate combination which the lime forms with the water; and in practical chemistry, and many of the chemical arts, it admits of numerous applications from its chemical agencies. It is highly corrosive, erodes and dissolves animal matter, and hastens the decomposition of a number of vegetable products.

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CHAP. IV.

## OF MAGNESIA.

**T**HIS earth, in the state of carbonate, had been employed in medicine, and had been considered as analogous to carbonate of lime. Hoffman observed, that it forms with sulphuric acid a salt very different from that formed by lime with the same acid. And Dr Black, discovering its principal properties, proved it to be essentially different from the other earths.

It is not much affected by galvanism, probably from the difficulty of rendering it a conductor of electricity. But when some of its saline compounds are submitted in the usual manner, in contact with quicksilver, to galvanic action, an amalgam is obtained, which appears to contain the metallic base of magnesia, as this earth is formed on its surface by exposure to the air. From this amalgam, Sir H. Davy found it difficult to expel the whole of the quicksilver, the glass tube in which heat was applied to it being acted on. In one experiment a solid was obtained, having the white colour and the lustre of the metallic bases of the other earths, which sunk rapidly in water, producing magnesia, and was also covered with a crust of magnesia on exposure to the air. In another experiment, on passing potassium over magnesia highly heated, and introducing quicksilver, an amalgam was obtained, from which any remaining potassium was abstracted by water, and a solid

metallic mass remained, which exposed to the air afforded a dry white powder, and when acted on by an acid gave a solution of magnesia. To the base of this earth the name of MAGNESIUM may be given.

Magnesia, under various states of saline combination, exists in nature in considerable quantity. It is found, in particular, in the water of the ocean, united with sulphuric and muriatic acids, and the same salts frequently exist in mineral springs. From either of them the magnesia, may be procured by decomposing them, by adding to their boiling solution an alkaline carbonate; the carbonate of magnesia is precipitated, and being thoroughly washed and dried, the carbonic acid is expelled from the magnesia by exposure to a red heat.

Magnesia obtained by this process is in the form of a white light spongy powder, very soft to the touch, inodorous, and having a slightly bitter taste. It slightly changes the blue vegetable colours to a green.

It is infusible when exposed even to the most intense heat. If previously made into a paste with water, it suffers contraction when exposed to a sudden heat.

It is insoluble in water; when dry, it absorbs a portion of water, but does not form with it a ductile paste. When it is precipitated from any of its saline solutions by potash, it retains in drying a kind of gelatinous consistence, by retaining water in weak combination. This forms perhaps a hydrate of magnesia, which, according to Davy, contains nearly a fourth of its weight of water. A hydrate appears to exist as a mineral production, composed of 70 of magnesia and 30 of water: it has a crystalline structure.

Magnesia combines with the acids: its salts are in general very soluble and crystallizable, and have a bitter taste,

They are decomposed by the fixed alkalis and by the alkaline earths, the magnesia being precipitated. Their decomposition by ammonia is partial, this alkali having a tendency to form with the magnesia and acid soluble ternary compounds.

It exerts no reciprocal action with the alkalis, nor with the alkaline earths. It combines by fusion with lime, and in the humid way it exerts an affinity to argil, combining with it and modifying its properties.

It combines, though very imperfectly, with sulphur, by fusion or by boiling, than in water. By sulphuretted hydrogen it is dissolved in small quantity. On the metals or metallic oxides it exerts no evident action.

Magnesia is scarcely applied to any use, except in medicine as an antacid and lithontriptic. Some of the native combinations of it with other earths have been used in the manufacture of porcelain, and prove useful by lessening the tendency to contraction in the baking of the earthy composition.



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## CHAP. V.

### OF ARGIL.

THIS earth is the base of the elays, whence the name of Argil has been given to it. Being the base of the salt, known by the name of Alum, it has also received the appellation of Alumina. The former is preferable, as less ambiguous. Though it exists in nature very nearly in a state of purity, forming the sapphire and some other gems, its state of aggregation in these forms of it disguises its chemical properties; and it is therefore as it is obtained by an artificial process that it is usually described.

The decomposition of this earth by galvanism has been very imperfectly effected. The usual methods proved unsuccessful, and Mr Davy obtained only imperfect indications by another method,—submitting the argil to galvanic action in fusion with potash or soda. The metallic matter obtained consisted principally of potassium or sodium; but with this was evidently combined a small portion of the base of the argil, for when it was oxygenated by water, it produced not only the alkali, but a minute quantity of this earth. By passing the vapour of potassium over the earth heated to whiteness, small particles of a grey colour and metallic lustre were obtained, which became white on exposure to the air.

The artificial process by which argillaceous earth is usu-

ally obtained, consists in dissolving common alum in water, and decomposing it by the addition of ammonia, which combines with the acid of the alum, and precipitates the argil which is its base. To this a little of the acid may however adhere; and to obtain the earth therefore in a state of perfect purity, the precipitate, after having been thoroughly washed, is redissolved in nitric acid, precipitated a second time by ammonia, and after being washed and dried, is exposed to a red heat.

Argil, obtained by these processes, is in the state of a light white powder, spongy and soft. It is peculiarly distinguished by forming with water a paste, which, when kneaded, is tenacious and ductile; and it is from the presence of this earth that the natural clays derive their plastic quality. Though no sensible quantity of it is dissolved by water, it forms with it an imperfect combination, the loose precipitate of argil, from the decomposition of its saline compounds, being somewhat gelatinous; and if diffused in a large quantity of water, it retains a portion of it in subsiding, and even in drying, forming a kind of transparent brittle mass; while, if precipitated from a concentrated solution, without being diffused in water, it forms, when dried, a loose powder. The latter has been named Spongy, the former Gelatinous Argil; it retains the water it has imbibed so strongly, that even exposure to a red heat does not entirely expel it. It is therefore a hydrate of argil, and appears to contain about 0.15 of water. A native hydrate exists containing a larger proportion.

The paste formed by kneading argil with water, contracts from the application of heat; the contraction, as has already been stated, in considering the application of this to pyrometry, continuing to proceed even at the most in-

tense heats long after the whole of the water has been expelled. The clay at the same time acquires a great degree of hardness from its augmented aggregation. In the intense heat of the most powerful burning mirror, argil does not melt; but the fusion of it in minute quantities has been effected by the heat excited by a stream of oxygen gas directed on burning charcoal.

Argil combines with the acids, neutralizing the acid properties. Those of its salts which are soluble have a sweetish, and, at the same time, astringent taste. They are decomposed by the alkalis and alkaline earths.

Argil combines more readily than the other earths with the alkalis. When its salts are decomposed by potash or soda, an excess of either added redissolves the precipitate of argil, forming with the acid a ternary compound. They can dissolve argil alone; and they form with it by fusion a species of combination, in which the argil is rendered soluble in water.

Argil exerts affinities to the other earths, both in the humid way and by fusion. Barytes and strontites render it soluble in water. Lime forms with it an insoluble compound, hence argil attracts lime from its solution in water, but the argil on the other hand renders the lime soluble to a certain extent in alkaline liquors. It also exerts an affinity to magnesia, in consequence of which it aids its precipitation from saline compounds. It unites in the humid way with silex, and, what is a singular effect, renders this earth soluble in acids. It also combines with it by fusion.

The combination of argil with silex by fusion, forms the basis of Pottery and Porcelain, at least these two earths form the essential ingredients, the argil communicating to the mixture that plastic quality, in consequence of which,

the paste formed with water, when thoroughly kneaded, can be fashioned and turned on the lath, the silex preventing this from contracting too much in drying, and by the action exerted between it and the argil, rendering the mixture capable of that species of vitrification which forms Porcelain. Natural clays, which are mixtures of these two earths more or less pure, are used in the manufacture, and require to be variously proportioned by intermixture. The composition is freed from impurities, is levigated to a great degree of fineness, and is kneaded with water into a ductile paste. This is turned on the lath into the requisite forms; the vessels are afterwards dried, and baked in a furnace with a fire gradually raised, and their surface is glazed by their being previously dipt into an earthy composition more fusible than that which forms the base. By the combination which the heat establishes, an imperfect vitrification is produced, forming a white semitransparent enamel, which constitutes porcelain, while the surface is more completely vitrified and rendered more smooth. Porcelain has the hardness and compactness of glass, is less brittle, and more capable of bearing sudden alterations of temperature, and has much beauty from its whiteness and semitransparency. The colours are usually formed from metallic oxides, which are mixed with fluxes to render them sufficiently fusible, and are applied by a pencil before the porcelain is baked.

The coarser clays, containing besides silex and argil, lime and iron, form the inferior kinds of porcelain and pottery. From their greater fusibility, they cannot sustain so high a heat, and are therefore glazed by more fusible materials, mixtures of earthy matter with glass, and often with oxide of lead.

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**CHAP. VI.****OF SILEX.**

**T**HIS earth is one very extensively diffused ; it forms the principal constituent part of a number of compound fossils ; and those in which it predominates having usually a considerable hardness, and the silex itself being altogether insoluble in water, and in its usual state of aggregation not easily diffused, it remains when they have been disintegrated or decomposed ; hence the sand of rivers and of the sea-shore is principally composed of it. Rock crystal, quartz, and flint, are fossils in which it exists almost perfectly pure, though in these its state of aggregation modifies its chemical properties, which are rather determined therefore from it in the state in which it is obtained by an artificial process.

The decomposition of silex has been imperfect. It is scarcely affected by galvanic action, and when submitted to it in fusion with potash, the metallic matter obtained when exposed to the air, or dropt into water, gave indications of the regeneration of silex, so as merely to warrant the conclusion that it had been decomposed, but without affording more than imperfect results.

The process by which Silex is usually obtained, consists in fusing calcined flint with three or four times its weight

of sub-carbonate of potash. The mass, when cold, is dissolved in water, and diluted sulphuric acid is added to the clear solution as long as any precipitation ensues; the precipitate is thoroughly washed with water, and dried. It appears, however, not to be pure silix, but to retain a portion of alkali in combination. Rock-crystal, pounded, probably affords it more pure, or the solution of silix in fluoric acid may be decomposed by ammonia, and the precipitate washed and dried.

Silix procured by precipitation is in the form of a light white powder, insipid, and gritty to the touch; when mixed with water, it does not form an adhesive paste. It is so infusible, as not to melt in the intense heat excited by oxygen gas directed on burning charcoal. It melts, however, in the flame of hydrogen and oxygen gases.

It is not dissolved in any appreciable quantity by water, yet there are facts which prove its solubility to a certain extent when this is not counteracted by its aggregation: if the solution of its compound with potash be decomposed by an acid, no precipitate appears, if the solution has been previously very largely diluted with water, though otherwise it would be apparent; and it exists in solution in some mineral springs, in which no substance that can contribute to its solution can be detected.

The earth is scarcely soluble in the acids, nor does it form with any of them neutral compounds analogous to those formed by the other earths and salifiable bases, a character by which it is peculiarly distinguished. By fusion it combines with boracic and phosphoric acid, forming a species of glass; when in a state of extreme division, muriatic acid appears to dissolve a small quantity. Fluoric acid is its proper solvent, dissolving it either when the acid

is gaseous, or when combined with water; though it is doubtful if the combination can be established so as to neutralize the acid.

This earth combines with the fixed alkalis. When boiled on it with water, a portion is dissolved, and by continuing the boiling, a gelatinous solution is obtained. By fusion, the combination is established perhaps more intimately, and the properties of the compound differ much according to the proportions.

When one part of flint or quartz is fused with three parts of sub-carbonate of potash, the carbonic acid is expelled, and the compound of silex and potash is partially soluble in water; with pure potash the combination is more perfect, and the compound more entirely soluble. The solution of silicated potash, or soda, *Liquor Silicum* as it is named, becomes gelatinous when concentrated by evaporation. When kept for a number of years, crystals have been observed to be deposited from it, transparent and hard. It is decomposed by all the acids, the siliceous earth being precipitated.

With a smaller proportion of alkali the compound is less soluble, and a stronger heat is required for its vitrification: it may even be obtained altogether insoluble, transparent, and possessed of considerable hardness. Such a combination constitutes *GLASS*, the essential parts of which are siliceous earth, and potash or soda. The proportions are about two parts of the earth, to from one to one and a half of the sub-carbonate of potash of commerce: they are intimately mixed, and the mixture is exposed to a heat sufficiently strong to expel the water and carbonic acid, and effect an imperfect combination. This is completed by afterwards applying a stronger heat, so as to produce

perfect fusion, the impurities and unvitrified matter being drawn off. The glass thus formed is more transparent and colourless, as the materials have been pure. Green glass is prepared from sand and kelp, or the residuum of the soap-makers' ley; white crystal glass, as it is named, is prepared from pounded flint or a very white sand; and to this, there is an addition of oxide of lead to promote the vitrification, and add to the density, and also increase the lustre by giving a higher degree of refractive power. A little oxide of manganese is added to remove the green tint liable to be produced from the presence of oxide of iron.

Glass in fusion has a great degree of tenacity and ductility, so that it can be easily cast in a mold, and cut and wrought in a variety of shapes. It loses this in cooling, and if cooled hastily is so brittle, that the slightest impulse or agitation is sufficient to cause it to fall into fragments. This is in part prevented by slow cooling, by which a different arrangement of the particles of the glass is allowed to be assumed. On this depends the advantage derived from the annealing of glass, as the process in which this slow cooling is conducted is named. It appears, even, that if the cooling be performed very slowly, the particles pass into such an arrangement that the glassy character is entirely lost, and the mass becomes opaque, and displays in its fracture a crystalline structure. Glass thus de-vitrified, may have its transparency and other usual properties restored by melting it, and cooling it more quickly.

Glass when prepared without an excess of alkali, is permanent in the air, and is scarcely acted on by any chemical agent. Fluoric acid, from its action on silicic acid, erodes and even dissolves it. The fixed alkalis fused with it render it soluble in water; and the metallic bases of the alkali-



lis decompose it, by partially abstracting the oxygen of the alkali, which enters into its composition, and perhaps also of the silix itself. When glass is exposed to heat, imbedded in various earthy mixtures, it loses its transparency, and forms a matter similar to porcelain, more hard, less fusible, and better capable of bearing sudden alterations of temperature than transparent glass, changes depending partly perhaps on the operation of slow cooling connected with the process.

Glass made from very pure materials, with the addition of borax and oxide of lead, and coloured by the addition of other metallic oxides, forms imitations of the gems. The transparency and colours of these are often equal to those of the real gems, but they are greatly inferior in lustre and hardness.

Silix exerts affinities to the other earths, and combines with the greater number of them by fusion, forming glasses generally more or less opaque. These affinities too are frequently exerted in the humid way. Thus silix is precipitated from its solution in potash, by the attraction exerted to it by barytes, strontites, and lime.

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## CHAP. VII.

### OF ZIRCON.

THE earth to which this name has been given, was discovered by Klaproth in a fossil, the Zircon or Jargon, brought as a gem from Ceylon. It has since also been discovered in the Hyacinth. It is obtained from the zircon by calcining it repeatedly to diminish its force of aggregation, reducing it to fine powder; and then fusing it with six times its weight of potash: the fused matter is dissolved in water, and to the solution muriatic acid is added, boiling it for a short time to precipitate more effectually the silix, with which the other earth is combined. The filtered liquor is decomposed by the addition of carbonate of soda; and the carbonate of zircon which is precipitated from it is dried, and the carbonic acid is expelled by heat.

This earth, submitted to the action of galvanism, in contact with potassium, affords metallic matter, which, when decomposed by water, afforded a minute portion of a powder, having all the characters of zircon. It appears, therefore, to be similar in constitution to the other earths, though the results are too imperfect to discover the properties of its base.

Zircon, obtained by the above process, is a white powder, insipid, and rough. When exposed, imbedded in charcoal, to the violent heat of a forge, it undergoes a se-

mi-vitrification; becomes so hard as to give fire with steel; has a brilliant vitreous fracture; and is of a grey colour. Its specific gravity in this state is 4.3. When the powder is mixed with water, it imbibes it, and forms a semi-transparent jelly, and it retains so much of this in drying, as to form a substance in appearance like gum. This is probably a hydrate of zircon: it appears to contain about 0.20 of water.

Zircon combines with the acids, and forms salts in general sparingly soluble. Those which are soluble have a sweetish astringent taste. Its affinities to the acids appear to be weak, as its salts are in general decomposed by a low heat, as well as by the alkalis, and all the other earths.

Zircon is insoluble in the liquid alkalis, but is dissolved by the alkaline carbonates. Its relations to the earths are scarcely known. It may be fused with silex and with argil, and a mixture of these three earths is more fusible than a mixture of two of them. It appears to combine too by fusion with some of the metallic oxides. On the simple inflammables it exerts no action.

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**CHAP. VIII.****OF GLUCINE.**

**T**HIS earth was discovered by Vauquelin, forming a constituent part of the beryl and of the emerald. He gave it the name of glucine, derived from the property it has of forming salts having a sweet taste. The process by which he obtained it from the beryl, was to fuse one part of it with three parts of potash; the mass, after cooling, was diffused in water, and dissolved in muriatic acid: the solution is evaporated to dryness, and, on again dissolving the matter in water, the siliceous present remains undissolved. The solution is decomposed by sub-carbonate of potash: the precipitate is digested with a solution of pure potash; the greater part of it, consisting of argil, together with a portion of glucine, is dissolved; but there remains a portion undissolved, which is the glucine, sometimes coloured by a little oxide of iron.

Mr Davy, in attempting the decomposition of Glucine, obtained results similar to those from zircon, an amalgam being formed, when it had been placed in the galvanic circuit with mercury and potassium which decomposed water, and which reproduced glucine, when the alkali in the liquid was neutralized by an acid. A similar result was obtained on submitting it to the action of potassium at a high temperature.

Glucine obtained pure is white, soft to the touch, and adheres a little to the tongue; it is insipid; is infusible; insoluble in water, but forms with it a paste which is somewhat ductile; this paste is not hardened by heat, nor does it contract. Its specific gravity is 2.96.

Glucine combines readily with the acids; its salts are generally soluble, and have a sweet taste.

They are decomposed by the alkalis: the earth is even completely precipitated by ammonia, a test which distinguishes it from argil, to which it has otherwise some resemblances. It is soluble in the fixed alkalis, but not in ammonia; it is dissolved, however, in carbonate of ammonia, forming a triple salt,—a property so far characteristic of it, though possessed also by zircon. It is dissolved also by the other alkaline carbonates. It decomposes the salts of argil. Its relations to the other earths are not known. Its salts are not precipitated by the alkaline prussiates. With borax it melts into a glass.

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## CHAP. IX.

### OF ITTRIA.

THIS earth was discovered by Gadolin, a Swedish chemist, in a fossil found at Ytterby in Sweden, since named Gadolinite, in which it is combined with silex and lime. It has also been discovered in some other fossils. In several of its properties it resembles glucine, but it differs entirely in others.

The process followed by Vauquelin to obtain the earth from the gadolinite, was to dissolve it with the assistance of heat in diluted nitric acid, pouring off the solution from the undissolved silex. The liquor is evaporated to dryness; the residuum being dissolved in water, the compound of nitric acid and ittria is obtained: ammonia is cautiously added; and after the separation of any oxide of iron in yellow flakes, a larger quantity is added, which precipitates the earth. The method followed by Klaproth of separating the iron by precipitation by succinate of soda, and precipitating the ittria by carbonate of soda, will probably afford it more pure.

Ittria is thus obtained in the form of a white powder, insipid; it is heavier than any other earth, its specific gravity being 4.842. It is not fusible alone, but with borax it forms a white glass. It is not soluble in water, but it retains that fluid with considerable force, and appears, therefore, to form a hydrate.

Ittria combines with the acids : its salts have generally a sweetish taste. Several of them too are coloured,—a property in which it differs from the other earths ; but, according to Eckberg, the colour arises from adhering metallic matter, principally manganese and iron. They are decomposed by the alkalis, by lime, strontites, and barytes.

Ittria is not dissolved by the liquid alkalis ; nor do they redissolve it when added in excess, after having precipitated it from its solutions, which distinguishes it from glucine. It is soluble in carbonate of ammonia, but it requires a quantity five or six times greater than glucine does. Prussiate of potash throws down from its solutions a granular precipitate, of a white or pearl-grey colour. It is precipitated in grey flocculi by the infusion of galls ; but very slightly by pure gallic acid. It is not affected by sulphuretted hydrogen, or hydro-sulphuret of ammonia.

The great specific gravity of this earth, and its being precipitated by the alkaline prussiates and by tannin from its solutions, in some measure connect it with the metals, and it probably ought to be regarded as a metallic oxide. It is not reduced, however, to the metallic state by heating it with charcoal, but it runs with it into a kind of semi-fluid mass, which is heavier than the earth itself. When submitted to the action of potassium at a high temperature, some appearances indicate the production from it of metallic matter.

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BOOK V.

## OF ACIDS AND THEIR BASES.

Acids form an order of chemical agents, distinguished by very appropriate characters, and extremely important in their chemical relations, partly from the numerous and powerful affinities they directly exert, and partly from the changes they produce in bodies by the communication of oxygen. They are compounds of inflammable bases with oxygen; and in conformity to the arrangement I have adopted, the chemical history of these bases is to be connected with the history of the individual acids.

Lavoisier inferred from an ample induction, that oxygen is the principle of acidity, communicating it to those compounds in which it predominates, and that acids are compounds of oxygen with combustible bodies. Sulphur, for example, combines with two proportions of oxygen, and in both forms acids. The case is the same with phosphorus, and with nitrogen; and charcoal also, in combining with the largest proportion with which it unites, forms an acid. The principal acids having simple bases were thus proved to be compounds of oxygen; and those which have compound bases, the acids, derived from the vegetable and animal kingdoms, were also proved to contain oxygen. Three acids, the Muriatic, Fluoric, and Boracic, had not been decomposed; but this, strictly speaking, formed no exception to the general principle, as analogy led to the



conclusion, that they also are compounds, and may contain oxygen as a common element.

More recent investigations, however, lead to some modification of the theory of Lavoisier. Substances have been observed to have the properties of acids, the composition of which is apparently demonstrated, and yet oxygen cannot be discovered in it: This is the case particularly with a compound of sulphur and hydrogen, Sulphuretted Hydrogen as it is named. This substance combines with the alkalis and earths, the most characteristic acid property, neutralizing the alkaline properties, and forming even crystallizable compounds; and it has also the property, the most delicate test of acidity, that of changing the vegetable blue and purple colours to a red. Yet analysis can discover no elements in its composition but sulphur and hydrogen.

There is one view under which this subject may be presented, which includes under it this apparently anomalous fact. Acidity, with all its characteristic qualities, has been considered as a property more peculiarly derived from oxygen. But it is possible that it may be derived rather from the bases which form acids,—being developed by their combination with any substance which communicates solubility, and of course greater energy of chemical action, provided that the substance producing this effect is not one which neutralizes acidity itself. Oxygen is the element that usually gives rise to this result: it renders soluble and active the bases of the different acids, and not neutralizing acidity, allows this property, if it is derived from the base, to be brought into action. Hydrogen may, however, have a similar effect, and, as sulphur is the base which, when combined with oxygen, forms what may be regarded

as the strongest acid, its acidity may also be rendered sensible by hydrogen, though to a less extent.

Some important results have been established with regard to the influence of Water on the property of acidity. All the more powerful acids contain a portion of it intimately combined. Sulphuric acid, nitric acid, muriatic acid, and phosphoric acid, contain nearly one-fourth of their weight of this combined water, and it cannot be expelled from them by heat: they are volatilized along with it, and even at a red heat, to which phosphoric acid can be submitted, it retains this combined water. Neither can they be formed without its presence by the combination of their constituent principles, nor can they be disengaged from compounds in which they exist without it be supplied. It is necessary, therefore, to their existence in an insulated form, and when combined with substances which do not neutralize acidity, as, for example, when combined with each other free from water, their acidity is not apparent, even by the most delicate test, that of reddening the vegetable colours, until a portion of water is added, when it is immediately developed. The rationale of some of these facts is not easily given, but they display the important chemical agency of water, a subject which is still not yet well understood.

Sir H. Davy has considered the facts with regard to the agency of water, so far as it is connected with one of these acids, the muriatic, under another point of view, which has led to the hypothesis of another acidifying element besides oxygen. Muriatic acid, like sulphuric acid, or nitric acid, holds a portion of water in intimate combination in its insulated state, and the real acid cannot be disengaged from compounds in which it exists, unless this water be

supplied. Muriatic acid, however, has also the singularity, that it cannot be decomposed by processes similar to those which decompose the others, no doubt from the strength of affinity between its elements; hence its composition cannot be demonstrated by analysis. It has the farther peculiarity, (probably from the same cause, the strong affinity of its base to oxygen), that it combines with oxygen, forming a compound which, existing in the gaseous form, has been known by the name of Oxymuriatic Acid Gas. When this gas is mingled with an equal volume of hydrogen gas, they act on each other when heat is applied, and the product is muriatic acid gas; the hydrogen gas, according to the common doctrine, entering into combination with the oxygen of the oxymuriatic gas, and forming water, which the muriatic acid gas holds combined with it in the gaseous form. There is another explanation, however, which may be given of the experiment, and of an extensive series of facts connected with the relations of muriatic and oxymuriatic acids;—that oxymuriatic acid is a simple substance, and that muriatic acid is a compound of it with hydrogen, an explanation of course involving the conclusion, that oxygen is not the sole principle of acidity, but that oxymuriatic gas is an element belonging to the same class. This opinion has been defended by Sir H. Davy. It will afterwards fall to be considered; at present it is sufficient to remark, that it rests on no conclusive evidence, and has no superiority over the common doctrine in its explanation of the phenomena, but is less simple, and at variance with very strict and extensive analogies.

The following are the properties characteristic of the acids. They are all sour to the taste; they change the

blue, purple and green colour of vegetables to a red ; they in general have a considerable affinity to water, and combine readily with it ; they dissolve the metals ; and they combine with the alkalis and earths, forming compounds, in which, when the due proportion is observed, the properties of the acid and of the salifiable base with which it unites are mutually lost.

The last property, that of neutralizing the properties of alkalis, is the one most eminently characteristic of acids ; and these two orders of chemical agents may be considered as in their chemical relations opposed to each other, the one always weakening the powers of the other. In combining, the acidity is diminished in proportion to the power and the quantity of alkali added : the property of alkalinity is equally weakened in proportion to the quantity and power of the acid brought into combination ; and in all these cases there is a certain proportion of acid and of alkali, in which, if the combination is established, the properties of neither are apparent, but are mutually neutralized. The compound formed at this proportion, is in chemical language named a Neutral Salt.

At the stage of neutralization it generally happens, that the compound has the greatest tendency to cohesion, probably from the condensation from the combination being greatest at that point. Hence it is more easily obtained solid by crystallization, or if it be less soluble, by precipitation, in this neutral state, than in any other. Sometimes, however, it has a greater tendency to crystallize or to precipitate with an excess of acid, or an excess of base, forming a compound in which there is such an excess, but in which a uniform and fixed proportion is established.

In all cases it has been supposed, that the combination of an acid with an alkaline base is limited to certain fixed proportions to that in which they are mutually neutralized, and in some cases to one or two others in which there is an excess either of acid or of base; and in these combinations the larger proportion of one of the ingredients is a simple multiple of the smaller proportion, as has been already stated (page 59). Potash, for example, or soda, combines with two proportions of carbonic acid, of which one is just double that of the other. Potash, too, combines with sulphuric acid, and with oxalic acid, in proportions in which the same law is observed. There are other saline compounds in which a similar arithmetical relation in the proportions seems to exist. The generalization, however, has been extended farther than the results of analysis strictly warrant: the deviations from the required proportions are often accounted for by hypothesis: there are cases where the law can scarcely be traced; and even where these relations in the proportions do exist, combinations of the same elements in other proportions having no such simple relation, and apparently indeed too numerous and indefinite to admit of it, can be formed. The most just view of the subject perhaps is, that an acid and alkaline base have a tendency to combine in every proportion, each weakening the properties of the other in proportion to its quantity and the energy of its action, though partly from the mutual attraction being exerted with more force in some proportions than in others, and partly from the operation of cohesion and other external forces, the combination is usually limited to certain proportions: these are more easily formed, and are more permanent; and in some cases the combination can be established in no others.

The relations of the acids to the earths is similar; they produce by their combination mutual neutralization of properties, and form compounds analogous to the alkaline neutral salts; while the combination is also not limited to this, but may be established so as to form compounds with an excess either of acid or of earth.

The different acids differ greatly in their power of neutralizing the alkalis and earths, so that to produce the state of neutralization very different quantities are required; and conversely the alkalis and earths differ as much from each other in their power of neutralizing the acids. According to the view given by Berthollet, the energy of the affinities of the acids to the alkalis and earths is indicated by their relative powers of producing this neutralization, the different substances being compared in the same relative weights; as the affinities of the different alkalis and earths to the acids may also be judged of from their power of neutralizing them,—the less of any of these substances, whether acid on the one hand, or alkali or earth on the other, which is required to neutralize a given quantity of another of the opposite order, the stronger being its attraction towards it. In the Appendix will be found the table of Kirwan, representing the relative quantities of the different acids, and the salifiable bases requisite to produce reciprocal neutralization.

The action of the acids on the metals is more complicated. An acid does not directly combine with a metal; the metal must always be oxidated. Hence, if it is not previously oxidated, the first action of the acid is to communicate oxygen, either a portion of that which it contains, or a portion of the oxygen of the water present, or of the atmospheric air; and with the oxide thus formed the acid

combines. The relation of the oxide is then the same as that of an alkali or earth to an acid ; they produce mutual neutralization of properties in the necessary proportions, and the compounds formed are perfectly analogous to neutral salts. They are named Metallic Salts.

The NEUTRAL SALTS, whether alkaline, earthy, or metallic, have certain properties as an order by which they are characterized which it is necessary to explain, as the history of these compounds, at least those of them formed from the alkalis and earths, is connected with that of the respective acids.

In general they are soluble in water, though they differ much in the degree of solubility : where more than 1000 parts of water are required to dissolve a salt, as the quantity is not appreciable, unless by very accurate experiment, such salts are regarded as insoluble. The solution of salts in water is augmented by increase of temperature, this weakening the force of cohesion, which counteracts the power of attraction exerted by the water to the salt ; and from the various forces of cohesion in different salts, the solvent power is very unequally increased by the same augmentation of temperature.

A salt may be recovered from its solution by evaporation of the whole, or of part of the solvent. If the evaporation is not carried too far, so that cohesion is forcibly and irregularly exerted, producing merely aggregation of the particles, the salt is procured in a crystallized form, that is, in small masses, transparent, and of regular geometric figures, denominated Crystals. Each salt takes on a figure peculiar to it, and hence the figures of the crystals serve to distinguish them, though these are also liable to be varied by circumstances. Some salts are crystallized

with difficulty ; while, with regard to others, the crystallization is easily affected, and the figures are regular. By slow or spontaneous evaporation, more regular and larger crystals are formed, than when it has been hasty. The solution which remains after a salt has crystallized, contains a portion of the same salt, which by a second evaporation may be obtained crystallized.

Crystallized salts always retain a portion of water, which is essential to the crystal, the transparency and cohesion being lost when it is abstracted. The quantity is very various, and is in some cases large, amounting to more than the weight of the real salt. Even those saline compounds which are not crystallized, but from their insolubility are precipitated at their formation, retain a portion of water in combination, and a similar portion remains even after what is more peculiarly considered the water of crystallization of crystallized salts has been expelled : nor can this combined water be expelled by the most intense heat.

From their relations to water, neutral salts derive some distinctive properties. Some liquefy, from the application of a moderate heat, owing to the solvent power of their water of crystallization being augmented ; and when this is dissipated by a continuance of the heat, a dry mass remains. This is named the Watery Fusion of Salts, and takes place principally in those which contain a large quantity of water. Some, when heated quickly, decrepitate from the sudden conversion into vapour of the small quantity of water of crystallization they contain. The crystals of many salts lose their transparency from exposure to the air, are covered with a crust, and at length fall into powder. This is named Efflorescence ; it arises from the abstraction of the water of crystallization by the air. Other



salts attract water from the air, so as to become humid, and at length liquid. This property, named *Deliquescence*, arises from the strong attraction to water.

One of the most important problems in chemistry, is that of determining the composition of salts, and assigning the precise proportions of their constituent principles. It may be attempted either by synthesis or analysis. In the first mode, a given weight of base may be combined with as much acid as produces neutralization, and the weight of the solid salt may be determined by obtaining it by evaporation and exsiccation. In the second mode, the salt may be decomposed by adding a substance which combines, either with the acid or base, and forms a product which can be easily obtained insulated, and the composition of which is known. Both methods, however, are liable to considerable uncertainty, principally from the difficulty of determining the quantities of water contained in the acids and in the bases, and the quantity retained in combination in the compound salts.

When two compound salts, in the neutral state, are mixed together, so as to produce mutual decomposition, the two new salts which are formed are equally neutral. This was observed by Richter; and it is an important fact, both as leading to a general principle connected with the doctrine of definite proportions, and as being capable of being applied in the investigation of the composition of salts. It proves, as has been already stated (p. 79.), that such a relation exists between acids and bases, in the power of producing neutralization, that similar quantities of acid power will be required by the different bases, and similar quantities of alkaline power by the different acids, so that if an acid or a base is weak in power, a corresponding

larger quantity of it will be necessary to neutralize the substance with which it combines. Hence the quantity of acid which neutralizes a certain quantity of a base, will, when transferred to another base with which a different acid is combined, detach from it such a portion of this acid as will neutralize the quantity of base with which the first acid had combined, and the state of neutralization will thus continue. It affords, too, a mode of verifying the results of analysis with regard to the proportions; for if the proportions of the elements of the salts, in which these double decompositions take place, have been assigned from analysis, they give of course the quantities requisite to produce neutralization: we can calculate, therefore, from these, whether the quantities in the salts decomposed, and in the new salts formed, are in such relative proportions as are necessary to continue this state of neutralization, and, of course, whether the proportions have been accurately determined.

Another law has been announced by Gay-Lussac, which may be applied to the determination of the composition of metallic salts,—that the quantity of acid in the salt is directly as the quantity of oxygen in the oxide which is its base. The fixed alkalis and the earths being probably metallic oxides, the same law may be applied to their combinations, and of course to the whole class of salts, with the exception of the ammoniacal ones. And as the proportions of oxygen combined with the metals are determined by methods different from those by which the proportions of acids combined with the oxides are ascertained, the one mode of analysis may be applied to determine the accuracy of the other. There are some grounds for doubt, however, whether the law is universally just.

It remains to explain the nomenclature of the acids and of the compound salts which they form.

Acids being regarded as compounds of oxygen with certain bases, the name of each acid is derived from the base of which it is formed. But as this base is often capable of combining with two proportions of oxygen, and of forming two acids different from each other, these must be distinguished, and this is done by a variation in the termination of the name, the syllable *ic* being the final one, when the acid is the one which contains the larger proportion of oxygen, and *ous* where it contains the smaller proportion. Thus sulphur, by combination with oxygen in two proportions, forms two acids; the term Sulphur is the radical whence their names are derived; the one, that with the less dose of oxygen, is the Sulphurous Acid; the other, the Sulphuric. We have thus also the Phosphorous and the Phosphoric, Nitrous and Nitric, &c. Where the base gives rise to only one acid, the name terminates in *ic*, as in the example Carbonic Acid. The acids from the vegetable and animal systems, having a compound base, the name cannot be derived in this manner, but is taken from the substance from which they are formed or prepared, as the Citric, Malic, Prussic, &c. A portion of water, it has been stated, exists in intimate combination in the more powerful acids. To distinguish them in this state from the real acid, it has been proposed to prefix the term *hydro* to the usual name, as hydro-sulphuric, hydro-nitric acid.

The nomenclature of the salts, formed by the union of the acids with the alkalis, earths, and metallic oxides, is equally systematic. All the salts formed from one acid are considered as a genus, under which are placed as

species the individual salts, formed by the union of that acid with these different bases. The generic name is derived from the name of the acid; the specific name from that of the base. When the name of the acid of which the salt is composed is that which terminates in *ic*, the final syllable of the name of the salt is *ate*; when the name of the acid terminates in *ous*, that of the salt formed from it has the last syllable *ite*. Thus, all the salts formed from sulphuric acid constitute a genus to which the name Sulphate is applied, and the species are designated by the addition of the name of the base, as Sulphate of Soda, Sulphate of Lime, Sulphate of Iron. Those, again, formed by sulphurous acid, are named Sulphites, as Sulphite of Ammonia, &c. On the same principle, we have Nitrates and Nitrites, Phosphates and Phosphites, Muriates, Carbonates, &c.

Salts are sometimes formed with an excess of acid or of base; to denote these a method proposed by Dr Pearson has been adopted. The genus being formed from the acid, when there is an excess of acid, the epithet *super* is prefixed to the name, when a deficiency of acid, the epithet *sub*. We thus speak of the Super-sulphate of Potash, the Sub-carbonate of Soda, &c.

Where an acid is united with two bases, as is sometimes the case, the names of both bases enter into its designation,—as the Sulphate of Argil and Potash, or the Tartrate of Potash and Soda.

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## CHAP. I.

### OF NITRIC ACID AND THE OTHER COMBINATIONS OF NITROGEN WITH OXYGEN.

**N**ITRIC Acid, long known to chemists in a state of greater or less purity, is a compound of oxygen and nitrogen. The properties of nitrogen having been already considered, the history of the acid, and of the other compounds which nitrogen forms with oxygen, remains to be delivered under this chapter. With a smaller proportion of oxygen than what enters into the composition of nitric acid, a compound is formed, having no acid properties, denominated therefore Nitric Oxide. With a still smaller proportion, another compound of uniform composition is produced, named Nitrous Oxide. When nitric acid has imbibed a portion of nitric oxide, it acquires some peculiar properties, and in this state has received the distinctive appellation of Nitrous Acid; which some chemists have likewise regarded as a compound in which oxygen and nitrogen are in direct combination in specific proportions. When the proportions of the elements of these compounds are reduced to volumes, they afford a striking illustration of the law observed by Gay-Lussac to regulate the combinations of elastic fluids, already stated, (p. 60.), nitrous oxide being composed of 100 of nitrogen with 50 of oxygen, nitric oxide of 100 with 100, and nitric acid, there is reason to believe,

of 100 of nitrogen with 200 of oxygen, all of them simple proportions by volume. This last number, however, is rather doubtful.

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### SECT. I.—Of Nitric Acid.

THIS acid being capable of being extracted without much difficulty from common nitre, had been long known to chemists, and in a diluted state had been used in the chemical arts, under the name of *Aqua fortis*. Priestley observed its partial decomposition, and its reproduction from the union of nitric oxide, the product of that decomposition, with oxygen. Cavendish discovered its ultimate composition, and proved that nitrogen is its base.

This was done by a very simple experiment,—taking the electric spark for a considerable time in atmospheric air, confined in a tube. The volume was diminished, an acid was produced, and this acid was found to be nitric. If a portion of oxygen gas were added to the air, and the electric spark continued sufficiently long, the disappearance of the whole was nearly complete; and a similar result was obtained, from submitting to experiment a mixture of oxygen and nitrogen gases. In all these cases, the electric spark establishes the combination of the gravitating matter of the two gases; and the principal peculiarity which attends this combination is the slowness with which it takes place, and its not being accompanied with any sensible extrication of heat or light.

Analysis likewise establishes the composition of nitric acid. If it be passed through an ignited glass or earthen

tube, it is resolved into oxygen and nitrogen gases; its saline compounds exposed to a red heat, afford the same elements; and its oxygen can be abstracted by inflammable substances, its nitrogen being evolved either pure, or retaining a portion of oxygen combined with it, which, by farther operations may be abstracted.

The proportions of its principles have been variously stated. Those assigned by Cavendish were 72.2 of oxygen, and 27.8 of nitrogen by weight. Mr Davy stated them not far different from these, at 70.5 oxygen, and 29.5 of nitrogen. The latter are not far from the proportions of 100 of nitrogen and 200 of oxygen by measure: from the law which appears to regulate the combination of elastic fluids, that it takes place in simple proportions by volume, there is some reason to admit these as the proportions. Gay-Lussac, accordingly, from the known composition of nitric oxide, and the quantity of oxygen with which he finds it to combine to form nitric acid, states the proportions at 100 of nitrogen and 200 of oxygen by measure, or 30.5 of the former, and 69.5 of the latter by weight. Some chemists, however, consider this as still doubtful: and the proportion of nitrogen has even been stated so low as 100 by volume to 250 of oxygen, or by weight 26.5 to 73.5.

Nitric acid is obtained from the decomposition of nitre, a salt in which it exists combined with potash, and the process usually followed is that by the medium of sulphuric acid. Two parts of nitre in coarse powder are put into a retort, and rather more than one part of sulphuric acid is poured upon it, the retort being placed in a sand bath, and connected with a large receiver. A moderate heat is applied to produce distillation, towards the end is gradually

raised, and is continued as long as any acid is produced. The sulphuric acid combines with the potash of the nitre, and disengages the nitric acid, this decomposition being aided by the greater volatility of the nitric acid. The nitric acid, however, when disengaged, is also partially decomposed; losing a little of its oxygen, a portion of it passes to the state of nitric oxide, and this being absorbed by the acid which distils over, gives it a yellow colour more or less deep, or converts it into nitrous acid. This decomposition appears to arise in a great measure from the action of the high temperature, and hence it takes place principally towards the end of the distillation. The addition of more sulphuric acid than is strictly necessary to neutralize the potash of the nitre is useful, partly from the quantity aiding its affinity, and partly by affording water to preserve the constitution of the nitric acid.

In consequence of this partial decomposition, an additional process is requisite to obtain nitric acid. The coloured acid is exposed to a gentle heat, applied by a water bath; the nitric oxide holding a portion of nitric acid combined with it is expelled, and the acid becomes nearly colourless; or, what succeeds more completely, the nitrous acid is distilled from a little oxide of manganese, which imparting to it oxygen, converts it into nitric.

Nitric acid is colourless and transparent; it emits white vapours, having a peculiar odour. It has all the acid properties, tastes sour even when much diluted, reddens the vegetable colours, and neutralizes the properties of the alkalis and earths. Its specific gravity in the strongest state in which it can be procured is 1.55 at 60°. In this state it contains a quantity of combined water, equal, according to



Kirwan and Dalton, to 26, in 100 parts. This, however, is not determined with perfect certainty. The presence of water is essential to the acid in its insulated state, as it can neither be formed, nor can it be disengaged from its saline combinations without water be supplied to it.

This acid freezes by cold, the facility of congelation varying considerably, according to its state of concentration: if it is highly concentrated, or if, on the other hand, it is much diluted, it freezes with more difficulty than when of intermediate strength. It is volatilized by heat; but its volatility is also much influenced by its state of concentration; the highest boiling point is that of the acid of the specific gravity of 1.42; it boils at  $248^{\circ}$ , if either stronger or weaker than this, it boils at a lower temperature. This, too, is the only acid which rises unchanged by boiling, a weaker acid becoming stronger, and a stronger acid than this becoming weaker as it boils. At a higher heat the acid is partially decomposed, and at the temperature of ignition, it is resolved into oxygen and nitrogen gases. A partial decomposition of it is also effected by light; oxygen is expelled, and it passes to the state of nitrous acid.

Nitric acid has a considerable affinity to water: it attracts it from the atmosphere, and it combines with it in every proportion. In consequence of this affinity, too, it acts with energy on ice and snow, liquefying them rapidly, and producing intense cold.

The affinity between the elements of this acid not being strong, it is decomposed by metallic and inflammable bodies which attract its oxygen partially or completely; and in consequence of this facility with which it yields oxygen, it acts with much energy on these substances.

It combines with the alkalis, earths and metallic oxides, forming salts, denominated Nitrates. These are all soluble in water and crystallizable; they have a cool penetrating taste; are decomposed at a high temperature, affording oxygen, and in consequence of this deflagrate, when heated with combustible bodies.

NITRATE OF POTASH is the salt well known by the name of Nitre or Saltpetre. In warm climates it is, under certain circumstances, formed spontaneously at the surface of the soil; it is thus procured in India, whence the nitre we use is imported. In some countries of Europe, the production of it is favoured by artificial arrangements. Vegetable and animal substances, with an intermixture of old plaster, mortar, or other forms of carbonate of lime, are put into ditches lined with clay, and covered with sheds to protect them from the rain, while the air is admitted. They are turned up occasionally, and at the end of a few months, when washed with water, afford nitrates of potash and lime. A quantity of wood ashes is added to the solution, the potash of which decomposes the nitrate of lime, and increases the product of nitrate of potash; this salt is obtained in crystals by evaporation, and is purified from a portion of muriate of soda and other saline matter which adheres to it, by repeated solutions and crystallizations.

The nitre does not pre-exist in these materials, and is therefore obviously formed in the process. As an intermixture of animal and vegetable matter, the presence of carbonate of lime and the admission of the atmospheric air are all necessary, it is probable that the nitrogen of the animal matter combines with the oxygen of the air, and perhaps with a portion of the oxygen of the vegetable matter, and forms the acid: the carbonate of lime favouring

this combination by the resulting affinity exerted by the lime, and attracting the acid as it is formed: the vegetable matter moderates the decomposition of the animal substances, and prevents their running into that putrefaction by which the nitrogen is spent in the formation of ammonia; it may farther afford the potash, which is the base of the nitre, though it has also been supposed that a part of this is formed in the process. A certain degree of humidity favours the mutual actions, whence these combinations arise, and diffuses more equally through the materials the nitrous salts.

Nitre crystallizes in six-sided prisms acuminated by six planes; its taste is cool; it is soluble in seven parts of water at  $60^{\circ}$ , a production of cold attending its solution, and in an equal weight of boiling water. It melts easily: if the heat be raised, a partial decomposition of the acid takes place, and oxygen gas is expelled; and at the temperature of ignition, the decomposition is more complete, and oxygen and nitrogen gases are disengaged. The proportions of its elements have been stated at from 51 to 53 of potash, with from 44 to 48.6 of acid.

From its facility of decomposition by heat, nitre produces deflagration, when heated with inflammable bodies, as has been explained under the general theory of combustion. It is from this that it is the principal ingredient in the composition of gunpowder, which consists of 75 parts of it by weight with 16 of charcoal, and 9 of sulphur. These ingredients are thoroughly mixed by continued trituration, a small quantity of water being added to favour this; the paste into which the composition is at length brought, is granulated by pressing it through a sieve, and the grains, after they are dry, are rounded and glazed by friction from agitation. The deflagration of the gunpowder, when an

ignited spark falls on it, is owing to the rapid communication of the oxygen to the sulphur and the charcoal, the sulphur in particular being easily inflamed; and its great expansive force depends on the sudden extrication of the aërial products,—sulphureous acid and carbonic acid formed by the oxygenation of the sulphur and charcoal, and nitrogen from the decomposition of the acid, probably with watery vapour, the elasticity of these being much increased by the caloric rendered sensible. Another detonating composition still more powerful than gunpowder, of which nitre is the principal ingredient, is that named *Pulvis Fulminans*. It consists of three parts of nitre, two of sub-carbonate of potash, and one of sulphur triturated together: when heated, it explodes with a very loud report. Its detonation appears to be owing to the formation of sulphuret of potash, which, re-acting on the water contained in the salts, disengages sulphuretted hydrogen, and this presented in its nascent state to the oxygen of the nitre, forms sulphurous acid and watery vapour in a state of high elasticity from the caloric disengaged.

NITRATE OF SODA crystallizes in rhomboidal prisms. Its taste is cool and penetrating; it slightly attracts moisture from the air; is soluble in three parts of water at 60, and in an equal weight of boiling water; it is scarcely so fusible as the nitrate of potash, but is decomposed by heat in the same manner, and, like it, excites deflagration when heated with inflammable substances.

NITRATE OF AMMONIA crystallizes in slender four-sided prisms, or, if the solution has been more concentrated in indistinct crystals, which form a compact mass, retaining less water of crystallization than the more regular crystals. Its taste is cool and bitter; it is deliquescent, and soluble

in two parts of cold water, and half its weight of boiling water. It undergoes the watery fusion, from a moderate heat, and the water of crystallization is expelled; if the heat is increased, it is decomposed, and if raised to ignition, there is detonation from the combination of the oxygen of the acid with the hydrogen of the ammonia. This happens at temperatures above 600: at temperatures between 300 and 500, the decomposition proceeds more slowly; the products are nitrous oxide and watery vapour, and it is from this decomposition that nitrous oxide is obtained in its purest form.

NITRATE OF BARYTES is obtained by dissolving the native carbonate in diluted nitric acid: it crystallizes on evaporation, in octaedrons, or in small brilliant plates: the crystals are not much altered by exposure to the air: they are soluble in 10 or 12 parts of water at 60°, and in 3 or 4 parts of boiling water. It is decomposed by heat, its acid being converted into oxygen and nitrogen gases. It detonates, but feebly, with inflammable bodies.

NITRATE OF STRONTITES is formed by pouring diluted nitric acid on the native carbonate. It crystallizes in hexaedral pyramids, or in octaedrons. This salt is soluble in its own weight of water at 60°; and at 212° it dissolves in little more than half its weight. It is deliquescent in a humid atmosphere; in a dry atmosphere it effloresces. It is decomposed by heat, and it deflagrates feebly, when laid on burning fuel.

NITRATE OF LIME is generally found in those situations in which nitrate of potash is formed. When its solution is evaporated to the consistence of a syrup, it affords slender prismatic crystals, deliquescent, and soluble in less than an equal weight of water at the temperature of 60,

and in still less boiling water. They are also soluble in alkohol. Exposed to heat, they undergo the watery fusion, and are decomposed, the acid being expelled. By having been heated it becomes phosphorescent, and retains this property when cold. When thrown on burning fuel, it melts, and detonates slightly.

NITRATE OF MAGNESIA has a taste bitter and acrid. Its crystallization exhibits a mass of small needle-like crystals: by spontaneous evaporation, it concretes in quadrangular prisms: it is deliquescent; is soluble in its own weight of water at 60°, and in half its weight of boiling water: it is also soluble in alkohol. By exposure to heat, it is decomposed.

NITRATE OF ARGIL.—The solution of argil in nitric acid becomes gelatinous on evaporation, and soft crystalline scales are formed, retaining generally an excess of acid: having a taste sour and astringent: easily soluble in water, and deliquescent. The nitrates formed from the remaining earths have been little examined, and are of no importance. The solution of ZIRCON in the acid affords a transparent resinous-like matter, not easily dried, having an astringent taste. That of GLUCINE cannot be crystallized, but by evaporation forms a gelatinous mass, which is very deliquescent. NITRATE OF ITTRIA assumes a gelatinous consistence by evaporation, and becomes brittle when this jelly cools. Its taste is sweet and astringent.

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**SECT. II.—Of Nitrous Acid.**

THE name of Nitrous Acid is given to the yellow acid obtained by the usual process of decomposing nitre by sulphuric acid; and it has been remarked, that it owes its yellow colour to the presence of a portion of nitric oxide. When this is disengaged by a moderate heat, it becomes colourless, and if nitric oxide is transmitted through it in this state, it regains its colour.

It appears to follow from these facts, that there is no acid of determinate composition to which the name Nitrous can be properly applied. What is called such is nitric acid holding nitric oxide dissolved: and the quantity of this may be variable, and even indefinite, between the minimum and maximum. According to the quantity communicated, the colour is deeper. From a portion not exceeding 1.2 of nitric oxide by weight in 100 parts, a pale yellow colour is communicated; this, as the quantity is increased, passes through shades of bright yellow to dark orange, in which the proportion amounts to about 5.5; beyond this an olive colour, and then a bright green, verging into blue, is obtained, and if the transmission of the nitric oxide gas be continued longer, it communicates its elasticity to the liquid acid, and the whole rises in very dense red suffocating vapours.

Some chemists have, however, assumed the existence of an acid of determinate composition, and have in particular given this name to the compound in which the largest proportion of nitric oxide gas is condensed by oxygen gas.

Gay-Lussac finds, that three volumes of the former is the largest quantity that can be condensed by one of the latter: he considers this, therefore, as the proper nitrous acid, and as nitric oxide consists of equal volumes of nitrogen and oxygen, it gives a compound composed of 3 measures of the former, and 5 of the latter. Mr Dalton finds that one measure of oxygen gas can condense, at the maximum quantity, 3.6 measures of nitric oxide gas. This compound too, Berzelius considers as nitrous acid, and states its composition at 37.4 of nitrogen, and 62.6 of oxygen. These combinations cannot, however, be established exclusive of the agency of water; and when its agency is admitted, the most probable view is, that it condenses the nitric acid, which, at the same time, combines with a portion of nitric oxide, condensed from the affinity exerted towards it, both by the acid and the water. The quantity of this varies as the water is more or less freely admitted, and there is no conclusive proof of the existence of a coloured acid containing fixed and specific proportions, considering its elements either as nitric oxide and oxygen, or nitrogen and oxygen.

In its gaseous form, nitrous acid forms a vapour of a very deep red colour, extremely suffocating; its specific gravity is 2.427, air being 1000; it is rapidly absorbed by water, forming a solution of a green colour. It acts on inflammables, and, in particular, sustains the combustion of phosphorus.

The liquid acid is more or less coloured according to the quantity of nitric oxide; its specific gravity is also diminished, a pale acid of 1.52, when converted into yellow acid, becoming nearly of the specific gravity of 1.51. The acid obtained by distillation from nitre and sulphuric acid



is usually of a pale yellow colour : but if the heat has been raised very high towards the end of the process, it is of a deeper colour ; and if any inflammable matter has been contained in the materials, it is of a dark orange red. The colours which the acid assumes from this impregnation of nitric oxide, are likewise dependant on its state with regard to dilution. If the dark orange-coloured acid be mixed with water, the different shades are produced, with a large quantity of water, blue, with more acid, olive, and bright green. These colours are not permanent ; the oxygen loosely dissolved in the water, or imbibed from the atmosphere, oxygenating the nitric oxide, and bringing the whole to the state of nitric acid.

Nitrous acid in its relations to other chemical agents is similar to nitric acid. It oxidizes in the same manner, and with the same phenomena, inflammable bodies and metals, and combines with the metallic oxides. These combinations are indeed merely those of the nitric acid, as the nitrous oxide is disengaged during the process.

The compounds of nitrous acid with the alkalis or earths can scarcely be obtained by direct combination ; for when it is added, the greater part of the nitric oxide is expelled. They are usually obtained by an indirect mode, pointed out by Scheele, that of exposing a nitrate to such a heat as partially decomposes the nitric acid, and expels part of its oxygen. The remaining acid with a portion of nitric oxide exists in combination with the alkaline base, forming the salts which have been named Nitrites. They are easily decomposed, give out nitrous acid vapour, on the effusion of air acid. On exposure to the atmosphere, they absorb oxygen, and return to the state of nitrates.

As the chemical properties and agencies of the nitric and

nitrous acids are so much alike, the latter is generally used in the arts, and indeed for most of the purposes to which the other might be applied, as it is more easily procured. The acid also, for the greater number of purposes for which it is used, must be diluted, and in this dilution it soon passes to the state of nitric. The *aqua fortis* of commerce is nitric acid diluted, and generally impure from the admixture of muriatic and sulphuric acids.

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### SECT. III.—Of Nitric Oxide.

FROM the action of diluted nitric acid on metals, an elastic fluid is disengaged, which was observed by Hales, and afterwards examined by Priestley, who gave it the name of Nitrous Air, or Nitrous Gas, a name not sufficiently distinctive, and for which, therefore, that of Nitric Oxide Gas has been substituted. It is a compound of oxygen and nitrogen, containing a smaller proportion of oxygen than nitric acid. Its formation in the above process, is due to the metal abstracting a portion of the oxygen of the acid, the nitric oxide assuming the elastic form. It is not always evolved pure, the abstraction of oxygen sometimes proceeding to a greater extent, and nitrous oxide or nitrogen gas being also evolved. It is obtained in the state of greatest purity in the action of diluted nitric acid on quicksilver or copper; one part of the concentrated acid being diluted with four or five parts of water, and poured on copper-filings in a retort; on applying a very moderate heat, the copper decomposes the acid by attracting oxygen, and nitric oxide gas is disengaged.

The relation of this elastic fluid to nitric acid is not only established by the nature of the process by which it is obtained, its composition is likewise established by its analysis. By taking the electric spark in it, it is converted into nitrogen gas, and nitrous acid. When exposed to the action of substances exerting a strong attraction to oxygen, it is partially or entirely decomposed. Thus by the action of iron or zinc, of phosphorus or charcoal, it is converted either into nitrogen gas, the whole of its oxygen being abstracted, or into nitrous oxide, part of it only being removed. From these analytic experiments, Mr Davy fixed the proportions of the principles of this compound at 56 of oxygen, and 44 of nitrogen by weight. This gives the proportions by volume of 54.5 with 50, not very different from that of equal volumes. By a new analysis of nitric oxide by potassium, Gay-Lussac accordingly finds it to be composed of equal volumes of oxygen and nitrogen, or by weight, 53.24 of the former, and 46.76 of the latter.

Nitric oxide is permanently elastic, colourless, and therefore invisible. It is rather heavier than atmospheric air, the proportion being 1.0388 to 1000. 100 cubic inches weigh 31.7 grains.

It proves extremely deleterious to animal life. Warm-blooded animals die almost immediately on a full inspiration of it, and the irritability of the heart is destroyed. Insects which live in several other noxious gases, are quickly killed by immersion in it, and fishes die in water impregnated with it. It proves even noxious to vegetable life, the leaves of a growing plant soon becoming withered in it, and the plant dying.

Exposed to distilled water, a portion of it is absorbed equal, when the water has been previously freed from air

by boiling, to about  $\frac{1}{4}$ th of the bulk of the water. The greater part, but not the whole of the gas is again expelled unchanged at a temperature of  $212^{\circ}$ . By common spring water, a larger quantity is absorbed, the nitric oxide being in part converted into nitric acid, by the oxygen which water holds loosely dissolved.

When the water is impregnated with certain metallic salts, as with the green sulphate or green muriate of iron, it condenses a much larger portion of nitric oxide gas. This has been supposed owing to a decomposition of the gas, its oxygen being attracted by the metallic salt; and in confirmation of this, it has been observed, that a portion of nitrogen exists in the residual gas. A portion of water, too, is decomposed, the hydrogen of which combines with the nitrogen, and forms ammonia. Davy, however, has affirmed, that the gas is merely absorbed: if the action of the atmospheric air be carefully excluded, he states that the liquid has no sensible acidity, and the nitric oxide gas may be procured from it unchanged, either by the removal of pressure by the air-pump, or by applying a very moderate heat. It is only if the air is admitted that nitric acid and ammonia are formed.

Nitric oxide gas has no acid properties. Its solution in water, freed from air, does not taste sour, nor does it red- den the vegetable colours. Neither does this happen from the introduction of the gas itself, previously washed in water, to vegetable coloured infusions. The colour, however, is impaired.

Nitric oxide gas is capable of supporting combustion in some substances only, and in them only at an elevated temperature. A lighted taper immersed in it is extinguished, as is sulphur introduced in a state of inflamma-

tion. Phosphorus may be fused in it without burning; but if introduced in a state of active combustion, it burns with splendour. Pyrophorus burns in it at a low temperature. Charcoal suspended in it, in a state of ignition, burns feebly.

With oxygen nitric oxide gas combines with great facility, and this forms its most important and characteristic property. They instantly combine, and a red coloured vapour is produced, which, if the experiment be made over water, is immediately absorbed, leaving, if the gases be pure, no residuum; and what is singular in so rapid a combination of oxygen, no sensible emission of light attends the combination, and so little caloric is rendered sensible, that the vessel scarcely becomes sensibly warm to the hand. The phenomena are similar when nitric oxide gas is presented to atmospheric air; the oxygen is condensed, and if the due proportions have been observed, the nitrogen of the atmospheric air remains pure.

From the application of this combination to eudiometrical experiments, it is an object of considerable importance to determine with precision the proportions in which these gases combine so as to produce mutual condensation. But this has been found very difficult; results extremely discordant have been given on different authorities, some fixing the quantity of oxygen condensed at 100, by 200 measures of nitric oxide gases; others finding that 250, or even 300 of the latter, are condensed by 100 of the former.

These differences arise from the circumstance, that oxygen and nitric oxide are capable of combining in different proportions, or if there is one proportion in which they are mutually saturated, the compound which results from this proportion is capable of absorbing variable proportions of

nitric oxide, and these are materially determined by the circumstances under which the combination takes place. The presence of water, in particular, by condensing the product, has a very important influence. If it is entirely excluded, as by combining the two gases in an exhausted globe, an elastic product of a red colour is formed, with a condensation of about half their volume, when two measures of nitric oxide and one of oxygen are combined. This æriform product may admit variable quantities of oxygen or of nitric oxide into the combination. If water be admitted to condense the elastic fluid, it does so during the progress of the combination itself, determines the proportions, therefore, in which this takes place, and renders these proportions different, as it is more or less freely admitted. The larger the surface of water is, over which the mixture is made, the less oxygen enters into combination with the nitric oxide, probably from the circumstance, that when a narrow surface of water is exposed to the mixture the absorption is slow, and the progress of the combination continues towards saturation, while, when the surface is large, it is absorbed as it takes place, and before the proportion in which the nitric oxide is saturated is fully established. And, on the same principle, agitation, and even the order in which the gases are presented to each other, have an influence on the results.

This property of nitrous gas of combining with oxygen gas at natural temperatures, and forming a compound quickly absorbed by water, has been applied to the purpose of eudiometry, and it has some advantages. The combination takes place so rapidly, that the result is immediately obtained, and it requires no complicated apparatus. It was introduced by Dr Priestley, and since his

time has been used in different forms. It has, however, been found liable to give different results from the influence of circumstances on the proportions in which the gases combine. They unite, as has been already remarked, so as to form either nitric acid or nitrous acid, or compounds intermediate between these, principally according as water is more or less freely admitted. If the water is presented in an extensive surface, as when the mixture of the gases is made in a wide tube, the smallest proportion of oxygen enters into the combination; while if it is less freely admitted, as by making the mixture in a narrow tube, the larger proportion combines. Mr Dalton has observed, that to give accuracy to the result as a eudiometrical process, the experiment must be conducted in such a manner as to form nitric acid or nitrous acid wholly, and without a mixture of the other. The former he has found to be most easily and most accurately effected. He adds to 100 measures of atmospheric air in a narrow graduated tube, (Fig. 23.), 36 measures of nitric oxide gas over water; avoids agitation; and when the diminution has ceased, observes its amount: this being multiplied by  $\frac{7}{9}$ , the product indicates the proportion of oxygen,  $\frac{7}{9}$ ths of the loss being due to its condensation. Gay-Lussac has affirmed, that the other mode of combining nitric oxide with oxygen, with the free exposure to water, is more uniform and accurate; and I have found, what is so far in conformity to this, that the simple method of Priestley, which is analogous to this, gives a very uniform result. He found, that 1 measure of oxygen is condensed by 2 measures of nitric oxide, when the experiment is made in this manner. Operating then on atmospheric air, let 100 measures of air measured by a narrow graduated tube be put into a

tube of  $1\frac{1}{2}$  inch diameter over water, and 50 measures of nitric oxide gas be added to it; on transferring the residual gas after a few minutes into the graduated tube, it will occupy a volume equal to 84; this gives a diminution of 66, which divided by 3 gives 22, as the proportion of oxygen by volume. As the method, however, under any form, is undoubtedly liable to fallacy, other eudiometrical processes ought to be preferred.

Another method of applying nitric oxide gas to eudiometry was introduced by Mr Davy, that of using solutions of sulphate or muriate of iron impregnated with it, these absorbing the oxygen of atmospheric air quickly, and producing a diminution equal to 21 in 100 parts. The method is too complicated for use, when we have others equally accurate and more simple.

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#### SECT. IV.—Of Nitrous Oxide.

THIS, the last of the compounds of oxygen and nitrogen, was discovered by Priestley, who gave it the name of Dephlogisticated Nitrous Air. Mr Davy, who examined it in a state of purity, and thus ascertained its most singular properties, gave it the more concise appellation of Nitrous Oxide.

It is obtained by various processes, in which nitric oxide or nitric acid is partially decomposed, as by exposing nitric oxide gas to the action of iron-filings moistened, of iron-filings and sulphur, or of the alkaline sulphurets; and



it is also disengaged in a state of mixture with nitrogen and nitric oxide during the solutions of some of the metals in nitric acid. But the process by which it is obtained most easily and in greatest purity, is in the decomposition of nitrate of ammonia by heat. This salt, in the different states of crystallization in which it exists, is decomposed, so as to afford this product at different temperatures, intermediate between  $320^{\circ}$  and  $500^{\circ}$ . Above  $600^{\circ}$  the decomposition takes place with an explosion, and the evolution of other products, principally water, nitrous acid, nitric oxide, and nitrogen gas. But this can be guarded against, by the due regulation of the heat applied by a lamp to the salt in a tubulated retort, raising it quickly to the requisite temperature, taking care not to exceed  $500^{\circ}$ , and, in particular, not to raise it so high as to produce a luminous appearance in the retort. The nitrous oxide gas with watery vapour are disengaged; the gas is received over water, as not much of it is immediately absorbed; it is generally opaque, from a small portion of nitrate of ammonia being volatilized; but this is soon absorbed by the water, and it becomes transparent.

In this process the nitric acid and the ammonia of the salt both suffer decomposition; the hydrogen of the ammonia attracts a portion of the oxygen of the acid and forms water, and the remaining oxygen is just sufficient, when combined with the nitrogen of the acid and the nitrogen of the alkali, to form this compound, nitrous oxide. Accordingly water and nitrous oxide gas are the sole products, if the temperature has not been raised too high to cause the operation of other affinities. The associated Dutch chemists had stated the composition of this gas at 62.5 nitrogen, and 37.5 oxygen. Estimating the propor-

tions from its formation, Mr Davy states them at 62.4 of nitrogen, and 37.6 of oxygen ; and from its analysis by detonation with hydrogen, or by burning charcoal in it at nearly the same, 63 of the one element, and 37 of the other. Converting these into volumes, they give the proportions of 100 of nitrogen and 49.5 of oxygen ; and Gay-Lussac has since found, that the exact proportion is that of 2 to 1, 100 parts of it affording by the action of potassium 100 measures of nitrogen and 50 of oxygen.

Nitrous oxide is permanently elastic. Its specific gravity is to that of atmospheric air as 1.614 to 1.000. 100 cubic inches weigh 50.1 grains. Its taste is sweetish. Its odour is very faint.

This gas is absorbed by water ; the water, at a mean temperature and atmospheric pressure takes up about half its bulk ; on boiling the solution, the gas is given out unchanged ; the solution has a sweetish taste, and a slight odour, not disagreeable ; neither it nor the gas changes the vegetable colours. It is likewise absorbed by alcohol and by ether, communicating a sweet taste ; and is expelled by heat, and in part by the addition of water.

Nitrous oxide gas suffers no diminution, nor any change when mixed with oxygen. At ignition, it detonates with hydrogen. It is decomposed at a high temperature, as by transmitting the electric spark through it, or passing it through an ignited earthen tube, and is converted into nitrous acid, and oxygen and nitrogen gases.

This gas is powerful in supporting combustion. A lighted taper burns in it with an enlarged and bright flame ; phosphorus with a dazzling white light ; sulphur with a vivid rose-coloured flame ; and iron-wire with corruscations. A higher temperature is required for these com-

bustions, than for the burning of the same bodies in oxygen gas or atmospheric air. During the combustion, a portion of nitrous acid is produced along with the product of the oxygenation of the combustible body.

The operation of this elastic fluid on the animal system, when it is received into the lungs, is scarcely analogous to that of any other physical agent. It had been believed to be, in common with the greater number of the gases, fatal to life. Mr Davy found that it could be breathed with safety, and in his farther experiments on it, discovered the singular effects it produces. After a few inspirations of it have been made, it causes a sense of lightness and expansion in the chest, and a pleasurable sensation begins to extend over the whole body; this increases, and is accompanied with a desire to inhale the gas; respiration therefore becomes fuller, and is performed with more energy. Exhilaration is soon produced; and if the respiration is continued sufficiently long, a crowd of indistinct ideas, often in very singular combinations, pass through the mind; there is an irresistible propensity to laughter and to muscular exertion, and violent exertions are made with alacrity and ease. These effects, after the inspiration has ceased, continue for four or five minutes, or sometimes longer; they gradually subside, and what is not the least of these singularities, the state of the system returns to its usual standard, and from this high excitement no subsequent languor or exhaustion is felt. Its operation is not however uniform on different individuals: its effects occur in various combinations; they are, as may be easily supposed, more readily excited in some than in others; and where much susceptibility has existed, alarming or unpleasant symptoms have been produced. Warm-blooded

animals confined in the gas, die in a few minutes, frequently with previous symptoms of excitement ; and fishes die in water impregnated with it. The gas appears during its respiration to be absorbed by the blood : this fluid acquires a purple colour, and after death the muscles are found inirritable. No satisfactory hypothesis can be advanced with regard to its operation.

Nitrous oxide can be combined with the fixed alkalis, by an indirect process discovered by Mr Davy,—exposing sulphite of potash or soda, mixed with pure potash or soda, to nitric oxide gas ; the sulphite attracts oxygen from the nitric oxide, and converts it into nitrous oxide, which, as it is formed, combines with the alkali, and the compound is separated by solution and crystallization from the other saline matter. These compounds, to which he gave the name of Nitroxides, are soluble and have a sharp taste ; they cause inflammable substances to burn or deflagrate when heat is applied, and afford nitrous oxide when decomposed by the acids, or by heat.

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## CHAP. II.

### OF SULPHURIC ACID AND ITS BASE.

SULPHUR is the base of sulphuric acid. When sulphur is combined with an inferior proportion of oxygen, it forms sulphurous acid. United with hydrogen in different proportions, it forms two compounds, sulphuretted hydrogen and super-sulphuretted hydrogen. It also unites with carbon. It farther combines with the alkalis and earths. The chemical history of all these substances forms the subject of the present chapter.

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#### SECT. I.—Of Sulphur.

THIS inflammable substance exists in the mineral kingdom, both in a state of combination, and in a pure form. In the latter state, it is principally a volcanic production, though native sulphur likewise occurs, which cannot be supposed to have this origin. It exists, too, in small quantity in vegetable and animal products.

Volcanic sulphur affords the greater part of the sulphur of commerce. It is usually purified by sublimation, and the sulphur is thus obtained in the form of a light powder of a yellow colour. This is easily fused, and forms a solid mass, brittle, and displaying somewhat of a crystalline

structure, and by slow cooling it may be obtained in needle-like crystals. By precipitating sulphur from its combination with an alkali by an acid, it is obtained nearly white, as it is also by dropping water on it when in fusion, or subliming it into a vessel filled with watery vapour; this whiteness has hence been ascribed to the combination of a small portion of water.

Sulphur melts at a temperature of  $224^{\circ}$ , and a phenomenon nearly peculiar to it is displayed in its fusion. If after it is melted, the heat be continued, or even raised, instead of flowing thinner, it becomes thick, and this continues progressive, as the temperature rises through a range of nearly 200 degrees, until it become quite viscid. The thickening, according to Dr Irvine's experiments, commences at  $226^{\circ}$  of Fahrenheit, and continues to increase to 550, at which temperature the sulphur sublimes. It is independent of the action of the air, and does not therefore arise from oxygenation; and indeed depends on no permanent change, as by reducing the temperature, the liquidity is recovered, and the experiment may be repeated on the same sulphur a number of times. If poured when viscid into water, it remains for a time soft and tough, and may be made to take the impression from a mould.

Sulphur rises in vapour, at a temperature not much higher than that at which it melts. If the air be admitted, it burns at a temperature of about 800, with a pale blue flame, and the production of pungent suffocating fumes. If the heat be raised, its combustion is more vivid, as it is also in oxygen gas.

In its combustion, sulphur combines with two proportions of oxygen, forming two acids. The principal product is a gaseous acid, Sulphurous acid gas as it is named;

but there is formed with this a portion of a liquid acid not volatile, containing a larger proportion of oxygen, the sulphuric acid. The proportions of these to each other are various, according to the circumstances of the combustion, the quantity of sulphuric acid being greater as oxygen is more freely supplied. The existence of an oxide of sulphur has been supposed, but is not clearly established.

Sulphur combines with hydrogen, and this combination, too, appears to be established in different proportions. It unites with phosphorus and carbon, and with the greater number of the metals. It combines with the alkalis and alkaline earths, acquiring from their action solubility in water and the power of decomposing it. It also enters into combination with their metallic bases: in its combinations with these as well as with some of the common metals, the phenomena of combustion are displayed.

Sulphur had usually been regarded as a simple substance. The younger Berthollet found, that on passing it in vapour through an ignited glass tube, traces of sulphuretted hydrogen are obtained: and, in combining sulphur with metals by applying heat, there is an evolution of the same product; it is likewise obtained by passing the vapour of water over melted sulphur, and that in this case it is not produced by the decomposition of the water, is proved by no portion of acid being formed. Hence the conclusion was drawn, that sulphur in its common state contains hydrogen. This appeared farther to be proved by some experiments by Mr Davy, with regard to the production of sulphuretted hydrogen, on submitting sulphur to galvanic action, or to the action of potassium at a high temperature. He farther inferred from some results, that oxygen exists in the composition of sulphuretted hydrogen,

and that it also must be combined in sulphur. Gay-Lussac and Thenard shewed the error of the conclusion with regard to the presence of oxygen in sulphuretted hydrogen, and the other results seem also to be doubtful. Berzelius has remarked, that when sulphur, perfectly dry, is combined with metals, there is no evolution of sulphuretted hydrogen. And even admitting them to be correct, they admit of explanation on the supposition which the phenomena do not preclude, that sulphur may contain a small quantity of combined water.

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#### SECT. II.—*Of Sulphuric Acid.*

SULPHURIC acid used to be obtained by distillation from sulphate of iron, the Green Vitriol of the older chemists, whence the name of Vitriolic Acid, by which it was known. It is now always procured from the combustion of sulphur; the method having been discovered of conducting this combustion, so that the formation of sulphurous acid is in a great measure prevented, and the principal product is sulphuric acid. The process consists in adding a small quantity of nitre,—from one-eighth to one-tenth, the weight of the sulphur. They are intimately mixed in powder, and portions of the mixture are successively kindled, and kept burning in a leaden chamber, the bottom of which is covered with water to the depth of three or four inches. The use of the nitre in this process was supposed to be merely that of sustaining the combustion, with the less free access of the atmospheric air. But its action appears to be more complicated and more important. The product of the com-



bination of sulphur with oxygen in combustion, is principally sulphurous acid: the nitric acid of the nitre, by the abstraction of its oxygen by the sulphur, yields nitric oxide gas, which diffuses itself through the chamber; it combines with the oxygen of the atmospheric air, and forms nitrous acid vapour, which in its turn yields a portion of oxygen to the sulphurous acid, and converts it into sulphuric acid, and thus the nitric oxide is the medium as it were by which the sulphurous acid is oxygenated, these actions being also facilitated by the affinity of the water present to the sulphuric acid.

The acid formed by this process is absorbed by the water in the chamber: when the liquor is sufficiently acid, it is removed, and by boiling it in glass retorts, a portion of sulphurous acid and the superfluous water are expelled, and it is brought to a state of concentration, having the specific gravity of 1.842. From the nature of the process, the acid is not perfectly pure: It contains a portion of sulphate of potash, derived from its action on the potash of the nitre, and perhaps also a minute quantity of sulphate of lead. These are in a great measure precipitated by diluting it with water, and are more completely separated by distilling it from a glass retort.

There is considerable difficulty in determining the proportions of oxygen and sulphur in sulphuric acid, principally from the difficulty of estimating the real product of acid free from water; and hence the results of different experiments have been extremely various. The proportion of sulphur has been stated so low as 42 in 100 parts, and so high as 72. This diversity has arisen principally from the estimation of the quantity of sulphuric acid, from the oxygenation of a given quantity of sulphur, having been

made by combining it with barytes, and from the fact not having been known, that this earth contains in its insulated state a portion of combined water. When allowance is made for this, it appears that 100 of sulphuric acid consists, according to those analyses that appear most correct, of 42.5 of sulphur, and 57.5 of oxygen. In any state of concentration in which it can be procured insulated, it has a portion of water always combined with it, and is therefore Hydro-sulphuric acid. At its usual specific gravity of 1.842, this is calculated by Kirwan to amount to 21, according to Dalton 24, in 100 parts. The greatest state of concentration in which it can be obtained, is, according to Dalton, of the specific gravity of 1.850; it then consists of 81 of real acid and 19 of water.

Sulphuric acid of the usual strength is somewhat viscid, and has an oily appearance. If pure, it is colourless and transparent; it is inodorous; its taste, when it is even largely diluted with water, is intensely sour, and in very minute quantity it reddens deeply the vegetable colours. In its concentrated state it is highly corrosive.

Sulphuric acid is congealed by cold, and even crystallizes with regularity. The temperature at which this takes place is very different, according to its concentration. When of the specific gravity of 1.843, it congeals at  $-15$ , but if it is diluted with half its weight of water, it requires a cold of  $-26$  to congeal it. There is a certain state of dilution most favourable to the congelation; this is when the acid is at the specific gravity intermediate between 1.786, and 1.775; at this it freezes at the temperature of melting snow; if either more diluted or more concentrated than this, the congelation requires greater cold to produce it. These facts are singular, and one not less so is,

that the acid remains congealed at a higher temperature than that necessary to cause its transition to the solid form. When sulphuric acid is impregnated with a portion of sulphurous acid, it becomes concrete even at common natural temperatures : this forms what was formerly called Glacial Oil of Vitriol.

Sulphuric acid boils at  $590^{\circ}$ . It is decomposed at a red heat, being resolved into oxygen and sulphurous acid.

It has a strong attraction to water, so that it imbibes it rapidly from exposure to the atmosphere. It combines directly with water in every proportion, the combination being attended with a considerable increase of temperature from diminution of capacity.

It forms no combination with oxygen or nitrogen : it absorbs nitric oxide, and acquires a purple colour ; it also unites with nitric acid, and this compound acid has the property of dissolving silver, while it does not dissolve copper : hydrogen decomposes it at a high temperature, by attracting its oxygen ; it sustains a similar decomposition from the primary inflammables ; any substance, for example, containing carbonaceous matter, acts on it even in the cold ; the acid becomes black from the evolution of charcoal, and a little sulphurous acid is formed. If heat be applied, the action is much more rapid, and carbonic acid and sulphurous acid gases are disengaged with effervescence ; a portion of sulphur may likewise be obtained.

The metals abstract oxygen from sulphuric acid, in general partially, so as to disengage sulphurous acid, the oxide combining with a portion of the acid that remains undecomposed. When the acid is diluted with water, it enables, by a resulting affinity, those metals which have a

strong attraction to water, to attract it from the water, and hence there is a disengagement of hydrogen gas.

Sulphuric acid combines with the alkalis, earths, and metallic oxides; producing when the due proportions are observed, mutual neutralization of properties. Its salts are named Sulphates. A considerable force of affinity is exerted between their constituent principles, and this is not much counteracted by any tendency of the acid either to elasticity or to cohesion, and hence they are not very liable to decomposition by the action of substances exerting attractions either to their acid or base. They are decomposed in general by heat: the metallic sulphates are more susceptible of this decomposition than the others, the acid being either expelled, or, by partial decomposition, converted into sulphurous and oxygen gases; the earthy at a higher temperature suffer a similar decomposition. The neutral alkaline sulphates are not decomposed, with the exception of sulphate of ammonia; but when crystallized with an excess of acid, part of that excess is by heat converted into the same products. They all suffer decomposition when heated with carbonaceous matter. Super-sulphates are also formed, and in a number of cases can be obtained crystallized, while there seems to be less tendency to the formation of sub-sulphates.

SULPHATE OF POTASH is formed by adding diluted sulphuric acid to a dilute solution of potash, or of carbonate of potash, until the acid and alkaline properties are neutralized. A more economical process, generally followed in pharmacy, is to prepare it from the residual mass obtained in the distillation of nitric acid from nitre and sulphuric acid, adding to it, dissolved in water, a solution of carbonate of potash, to neutralize any excess of acid, and

obtaining the sulphate by evaporation. The crystals of this salt are prisms, small and grouped; it requires for its solution seventeen parts of water at  $60^{\circ}$ , and five parts at  $212^{\circ}$ . Its taste is bitter. It is decomposed, like the other sulphates, by exposure to heat with carbonaceous matter. Acted on by nitric or muriatic acid, it suffers partial decomposition from the abstraction of part of the base, the decomposing acid acting by its affinity and quantity, and producing that participation which happens when two acids act on one base. It consists of 55 of potash, and 45 of acid. It can combine with an excess of acid, and even with this excess crystallizes; and from the experiments of Berthollet it appears even that compounds with various proportions of excess of acid may thus be obtained. These super-sulphates are considerably more soluble than the neutral sulphate; by the repeated action of water the excess of acid is almost entirely abstracted.

**SULPHATE OF SODA.**—This is the salt known by the name of Glauber's Salt, from Glauber the chemist, by whom its properties were first noticed. He obtained it from the residuum of the distillation of muriatic acid, from muriate of soda and sulphuric acid: this consists of the soda of the muriate of soda, with sulphuric acid in excess: it is dissolved in water; the excess of acid is neutralized by adding lime; the fluid is allowed to remain until it becomes clear, is drawn off in shallow leaden vessels, and on cooling affords the neutral sulphate in crystals. It is also obtained as a residuum in other processes, particularly in the preparation of sal-ammoniac from muriate of soda and sulphate of ammonia. It crystallizes in six-sided prisms bevelled at the extremities. Its taste is strongly saline and bitter. It is efflorescent; the crystals in a dry atmosphere

soon becoming white and opaque, and at length they fall into powder. It is soluble in less than three times its weight of water at  $60^{\circ}$ , and in less than its own weight at  $212^{\circ}$ . Exposed to heat it undergoes the watery fusion; the water of crystallization is soon dissipated, and by urging it with a strong red heat it may be melted. In its crystallized state it consists of 18.5 of soda, 23.5 of acid, and 58 of water. It suffers decompositions similar to those of sulphate of potash. Like it, too it can combine with an excess of acid, and according to Berzelius in various proportions.

SULPHATE OF AMMONIA crystallizes in slender six-sided prisms acuminate by six planes. It is soluble in about two parts of water at  $60^{\circ}$ , and in an equal weight of boiling water; is slightly efflorescent. Exposed to heat, it melts, and is decomposed, part of the ammonia being exhaled; at ignition its acid is decomposed. It consists of acid 55, ammonia 14, water 31.

SULPHATE OF BARYTES is formed when barytes is presented to sulphuric acid, in whatever state of combination either may previously exist. It is precipitated in powder, which is not soluble in water in any appreciable quantity. It is melted by a strong heat. When heated with carbonaceous matter, its acid is decomposed, and sulphuret of barytes is formed. The determination of the proportions of its constituent parts is of considerable importance, as it is usually employed as the mode of obtaining sulphuric acid free from water, in experiments made to estimate its quantity. The results, however, have been very discordant, principally from the presence of water in barytes not having been suspected. They are now fixed apparently with as much precision as the investigation admits, at 67 of

barytes, and 33 of acid, though still this cannot be perfectly correct, as it supposes the sulphate of barytes to be free from water, while, according to Berthollet, it retains a portion in combination. Besides this neutral salt, barytes can combine with an excess of sulphuric acid in various proportions; it forms a liquid that congeals into a congeries of prisms; this is decomposed, and the neutral sulphate is precipitated, on the affusion of water.

SULPHATE OF STRONTITES is in the form of a white powder, insipid, and so very sparingly soluble in water, as to require nearly 4000 parts for its solution. It consists of 42 of acid, and 58 of base. It too combines with an excess of acid, and is rendered more soluble in water, and crystallizable.

SULPHATE OF LIME, long known to chemists under the names of Gypsum and Selenite, is one of the saline substances most abundant in nature. It forms entire strata, is diffused in almost every soil, and is contained in almost all river and spring water, giving rise, when the quantity is considerable, to the quality of these named hardness. It requires about 500 times its weight of water for its solution at a mean temperature. At that of 212 it is more soluble, and this latter solution, upon cooling slowly, deposits minute crystals. Exposed to heat it appears to effervesce or boil, owing to the expulsion of its water; it becomes opaque, and falls into a white powder. This, diffused in water, speedily consolidates from a species of irregular crystallization. When exposed to a more intense heat, it vitrifies if any other earth is mixed with it. Heated on charcoal, or by the blow-pipe, it is partially decomposed, part of the oxygen of its acid being abstracted. It consists of 32 of lime, 46 of acid, and 22 of water;

when calcined of 42 of lime, and 58 of acid. Its principal use is in statuary, and in the formation of plaster or stucco work.

SULPHATE OF MAGNESIA is found in sea-water, and in many mineral waters, and is usually extracted from the brine of sea-water, Bittern as it is named, this being boiled down until it afford the sulphate of magnesia, on cooling, in acicular crystals; or sulphate of iron is added, the sulphuric acid of which combines with the magnesia of the muriate of magnesia, and increases the quantity of sulphate. Obtained in this way, it exhibits a confused mass of needle-like crystals, which are deliquescent, but this is owing to the admixture of muriate of magnesia, as the pure sulphate is rather efflorescent. By slow evaporation of its solution, it crystallizes in quadrangular prisms acuminate by four planes. These crystals are soluble in little more than their own weight of water, at the temperature of  $60^{\circ}$ , and in three-fourths of their weight of boiling water. They undergo the watery fusion at a very moderate temperature, and the dry mass which remains is melted in a strong heat, but is not decomposed. The crystallized sulphate consists, according to Kirwan, of 29.3 of acid, 17 of base, and 54 of water; according to Henry, of 37 of acid, 19 of magnesia, and 44 of water. The taste of this salt is very bitter, and the bitterness of sea-water and many mineral springs is owing in part to its presence.

SULPHATE OF ARGIL, formed by dissolving the earth in sulphuric acid, crystallizes when neutral, in scales white and of a pearly lustre, which alter little by exposure to the air: its taste is astringent: it is very soluble in water: when exposed to heat, its water of crystallization is dissipated, and, by a stronger heat, its acid is expelled. When



there is an excess of acid, the compound crystallizes with more difficulty, as, on evaporation, it assumes a gelatinous consistence. Small brilliant crystals, however, are formed in it.

The salt known by the name of Alum is a ternary compound of argil, potash and sulphuric acid, with an excess of acid; in some of the varieties of the alum of commerce, ammonia even enters into the composition, and it is often contaminated with a little sulphate of iron. Alum is a natural product, occurring efflorescent in the layers of what has been named Alum Slate; it is also formed by an artificial process, from what is named Alum Ore, which appears to be a variety of slate, impregnated with sulphur or sulphuret of iron; it is calcined, and afterwards exposed to the atmosphere in a humid state; the sulphur absorbing oxygen is converted into sulphuric acid, which acts on the argillaceous earth of the slate. The saline matter is extracted by lixiviation, and when a little potash has been added, alum is obtained by crystallization. The alum of commerce is in large masses, white and transparent. When regularly crystallized, the form of the crystals is an octaedron. It is soluble in 15 parts of cold, and in two parts of boiling water: its crystals are slightly efflorescent: its taste is sweetish and astringent. Its solution reddens the vegetable colours. When exposed to a moderate heat it melts, from the water of crystallization which it contains dissolving the solid salt; this soon evaporates, and leaves a light white powder, named Burnt or Calcined Alum. By a strong heat, the acid is partly expelled, partly decomposed, a quantity of oxygen being afforded by its decomposition. This salt is decomposed by the alkalis and alkaline earths, which attract the greater part of the acid,

and precipitate the earth with a small quantity of acid combined with it. It consists of acid 33, argil 11.7, potash 8.3, water 47. Vauquelin regards it as a compound of sulphate of potash and super-sulphate of argil.

The acid of alum is decomposed by heating it with carbonaceous matter.

A decomposition of this kind affords a very peculiar product, distinguished by burning spontaneously on exposure to the air. This substance, named Pyrophorus, is prepared by exposing to heat in an iron-pot, three parts of alum, with one part of flour: the mixture liquefies, and is to be stirred constantly till the whole becomes grey, and easily reducible to powder while hot. The coarse powder is put into a coated phial, so as nearly to fill it, and this, slightly stopped with clay, being surrounded with sand in a crucible, is exposed to a red heat, until a blue flame appears at the mouth of the phial: when this has continued ten minutes, the crucible is removed from the fire, and the phial, when sufficiently cold, is accurately stoppt.

Pyrophorus inflames in atmospheric air, especially in a moist atmosphere. It burns brilliantly in oxygen gas, in nitrous gas, and oxymuriatic acid gas, and is inflamed by sulphuric and nitrous acids. With regard to the theory of its combustibility, it has been proved, that in order to form it the alum must contain potash; the sulphuric acid is decomposed by the carbonaceous vegetable matter, and a portion of sulphur, which is its base, is supposed to combine with the potash, and form a sulphuret, which is diffused through the argillaceous earth, with a quantity of charcoal perfectly dry. When exposed to the air, moisture is absorbed, by which the temperature is raised: and the sulphur, it is supposed, absorbing oxygen, is inflamed,

and kindles the dry carbonaceous matter. It is not improbable, as Davy has suggested, that a portion of the potash may be decomposed by the joint action of the sulphur and charcoal, and potassium produced, to which the combustibility may be principally owing.

Alum is used in a variety of arts. It hardens tallow: it increases the adhesive power of the farinaceous pastes: it renders turbid water clear; and it is an essential article in the art of dyeing, fixing the colours, and often adding to their brilliancy. The presence of iron often injures the more delicate colours, and the superiority of the variety called *Roman Alum*, as a mordant, appears to be owing to its being free from this metal. Alum is also used in medicine as a powerful astringent.

The other sulphates have been little examined. *Sulphate of Zircon* is insipid and insoluble. *Sulphate of Glucine* is difficultly crystallizable; its taste is saccharine and astringent; it is very soluble in water, its solution assuming by concentration the consistence of a syrup. *Sulphate of Iron* crystallizes in small brilliant grains, of a rhomboidal form, and of a colour inclining to amethyst red. Their taste is sweet and astringent.

The remaining combinations of sulphuric acid fall to be considered under the history of the substances to which they belong. The acid itself is of extensive use. It is one of the most important agents in chemical investigations, either by the affinities it exerts, or by the oxygen it communicates. In the arts it is much employed, as in bleaching; in some of the processes of dyeing; in metallurgic operations, and in the preparation of neutral salts.

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### SECT. III.—Of *Sulphurous Acid*.

SULPHUROUS acid is formed in the slow combustion of sulphur, but it is mixed with a little sulphuric acid, and to obtain it pure, the easiest process is to decompose sulphuric acid by the action of substances which partially abstract its oxygen, and which do not form an aeriform product. The metals produce such a decomposition, and quicksilver or tin affords the purest product. One part of either is put into a retort, with two parts of sulphuric acid; heat is applied by a lamp; the metal attracts part of the oxygen of the acid, and the sulphurous acid gas is disengaged. Being absorbed by water, it is received over mercury.

The composition of sulphurous acid has been variously stated with regard to the proportions of its elements. There is reason, however, to believe, that oxygen gas in combining with sulphur to form it suffers no change of volume, but is merely increased in density by the addition of the sulphur. From knowing the difference, therefore, between the specific gravities of sulphurous acid gas and oxygen gas, the proportions may be assigned. From this mode of estimation, Sir H. Davy infers that they are equal weights. Gay-Lussac had stated them at 52 of sulphur and 48 of oxygen; Mr Dalton at 48 of sulphur, and 52 of oxygen. The proportion of equal weights is therefore just the mean of these.

This acid exists in the state of gas; but it has been re-

duced to the liquid state by the application of intense cold and pressure. Its specific gravity, compared with atmospheric air, is as 2.220 to 1.000; 100 cubic inches weigh about 68 grains. It has a suffocating pungent odour, proves speedily fatal to life, and instantly extinguishes combustion.

It is easily absorbed by water, 100 grains of water taking up 8.2 grains, equal to 33 times its volume. The solution has a pungent disagreeable odour, and an acid taste. It reddens some of the vegetable colours, while there are others, the colour of which it destroys. From the application of a moderate heat, the greater part of the gas is expelled, though the liquor remains acid, from the presence of sulphuric acid. It is singular that it is not expelled by freezing; it remains combined with the ice, and renders it so heavy that it sinks in water.

The liquid sulphurous acid absorbs oxygen from the atmosphere, and is converted into sulphuric acid. If they are mixed in the gaseous state, and a small portion of water is introduced, they gradually combine. By passing sulphuric acid through a tube heated to redness, a great part of it is decomposed, and the sulphurous acid and oxygen into which it is converted are obtained in the proportion of two parts by volume of sulphurous acid gas, and one of oxygen gas. Hydrogen, at the temperature of ignition, attracts oxygen from sulphurous acid. Charcoal, at the same temperature, produces a similar change, and sulphur is deposited. It is not decomposed by phosphorus, and it acts feebly on the metals. Nitric oxide gas does not act on sulphurous acid gas when they are dry; neither does nitrous acid vapour; but if to the latter mixture a little water be admitted, a solid crystalline com-

pound, according to Davy, is formed; and if more water is added, nitric oxide gas is given off, and the sulphurous is converted into sulphuric acid.

This acid combines with facility with the alkalis, forming salts denominated Sulphites. Their taste is sulphureous; they are decomposed by a high temperature, and by the greater number of the acids. The alkaline sulphites are more soluble than the sulphates in water, the earthy sulphites less so. All these salts are converted into sulphates by exposure to the atmospheric air, or by the action of any substance capable of affording them oxygen. They scarcely require individual notice. **SULPHITE OF POTASH** is obtained in crystals, white and transparent, of a rhomboidal figure, or in the form of small needles, soluble in an equal weight of water at a mean temperature, and in a less quantity of hot water.—**SULPHITE OF SODA** is white and transparent, soluble in four parts of water, more soluble in warm water; and the solution, on cooling, affords crystals of a prismatic form.—**SULPHITE OF AMMONIA** requires less than its own weight of boiling water for its solution, and the solution crystallizes on cooling; its crystals, being six-sided prisms, white and transparent.—**SULPHITES OF BARYTES and ARGIL** are insoluble; those of **LIME and MAGNESIA** soluble and crystallizable.

Sulphurous acid is used, from its property of destroying colours, to whiten silk and wool; it is applied usually under the form of the fumes of burning sulphur.

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SECT. IV.—*Of Sulphuretted Hydrogen, and other Compounds of Sulphur and Hydrogen.*

SULPHUR combines with hydrogen in various proportions. The compound best known is an elastic fluid, which has received the name of Sulphuretted Hydrogen. There appears to be another with a larger proportion of sulphur, which may be named Super-sulphuretted Hydrogen, and there is some reason to believe that this latter combination may be established in different proportions.

1. SULPHURETTED HYDROGEN.—This compound is not easily formed by the direct combination of its constituent principles, but is obtained by indirect processes, in which the hydrogen is presented to the sulphur in a condensed or nascent state. That which affords it with most facility is the action of diluted muriatic acid on a sulphuret of iron, prepared by combining by fusion one part of sulphur with three parts of iron. The acid diluted with four parts of water acts on this compound, by a resulting affinity; it enables the iron of the sulphuret of iron to decompose the water, by attracting its oxygen; the hydrogen is disengaged, and being presented in its nascent state to the sulphur of the sulphuret, combines with it, and forms the sulphuretted hydrogen, which passes into the elastic form. It is liable to be mixed with a little hydrogen gas. By applying heat to a mixture of muriatic acid and sulphuret of antimony, it is obtained purer, as it is also from the action of muriatic acid on the compounds which sulphur forms with alkaline bases.

Though it is difficult to combine sulphur and hydrogen together, so that the whole of the hydrogen is converted into sulphuretted hydrogen, a portion of the latter compound is always formed, and this takes place apparently without any change of volume, the hydrogen merely receiving as it were the sulphur into the space it occupies; the increase of density, therefore, shews the quantity of sulphur dissolved; and hence, from comparing the specific gravities of pure hydrogen, and of sulphuretted hydrogen, the composition of the latter may be inferred. Both from this mode of estimation, and from the decomposition of the gas by heating tin in it, which combines with the sulphur, and leaves the volume unchanged, the proportions appear to be 6 of hydrogen and 94 of sulphur.

The specific gravity of sulphuretted hydrogen gas, compared with atmospheric air, is 1.1912. 100 cubic inches of it weigh 36.5 grains. Its smell is extremely fetid and peculiar. It extinguishes combustion, and is incapable of supporting animal life. It is absorbed by water, the water taking up more than its volume, or 100 cubic inches absorbing, according to Dr Henry, 108, and acquiring from this impregnation the fetid smell of the gas, and a nauseous taste. It is colourless and transparent, but becomes turbid from exposure to the atmosphere.

In its elastic state, sulphuretted hydrogen does not combine with oxygen at a low temperature; but if placed over water, their mutual action is facilitated by its medium, the oxygen combines with the hydrogen, and a thin deposite of sulphur is formed. At the temperature of ignition the combination is more rapid. If the sulphuretted hydrogen gas be kindled in contact with the atmospheric air, it burns with a blue lambent flame. When previous



ly mixed with one or two parts of atmospheric air, it does not detonate, and the combustion of its elements is not complete, part of the sulphur being deposited on the sides of the vessel. When mixed with an equal volume of oxygen gas, and kindled, it inflames with detonation, the products being watery vapour and sulphurous acid. It is decomposed by the action of some other gases, which afford to it oxygen, as by sulphurous acid, and nitric oxide gas, the oxygen combining principally with its hydrogen, and sulphur being deposited: oxymuriatic acid gas likewise causes a precipitation of sulphur.

Sulphuretted hydrogen exerts a peculiar action on the metals. It tarnishes them quickly, or communicates shades of yellow, brown or purple, with a diminution of metallic lustre. It deepens the colour of their oxides, and if added to metallic solutions, it produces a precipitate of the metallic oxide or of the metal in combination with the sulphur, generally of a dark shade.

Sulphuretted hydrogen combines with the alkalis and earths, and displays in these combinations powers similar to those of an acid; it neutralizes the alkaline properties, and forms compounds capable of crystallizing, and having properties analogous to those of neutral salts. And not only has it these powers analogous to those of acids, it has farther the most distinctive character of acidity, that of reddening the vegetable colours; it at least reddens the colour of litmus or radish.

If this substance, therefore, be a compound of sulphur and hydrogen, it forms an exception to the universality of the proposition, that oxygen is the principle of acidity, and affords an example of an acid containing no oxygen. To obviate this conclusion, it has been supposed that

oxygen may exist in its composition, and some results, as has been already stated, connected with the action of potassium on sulphuretted hydrogen, were obtained by Sir H. Davy, from which he inferred the presence of oxygen, the potassium burning with a brilliant flame in the gas, and the product, when acted on by diluted muriatic acid, not yielding the proportion of sulphuretted hydrogen which it must have done had not oxygen been communicated to it. The reverse of this, however, has been found by Gay-Lussac and Thenard. There is, therefore, no experimental evidence of the existence of oxygen in sulphuretted hydrogen, and the obvious acid quality of this compound affords a confirmation of the view which I have already stated, (p. 365), that acidity is a property derived from combustible bases, developed only by substances which render these bases soluble and active, an effect which hydrogen may produce as well as oxygen. Hence sulphuretted hydrogen may display acid powers, though no oxygen exists in its composition.

The compounds of sulphuretted hydrogen with the alkaline or earthy bases, are formed by transmitting it in its elastic form through water, in which they are dissolved or suspended, continuing the transmission until they are saturated. They are named Hydro-sulphurets. They are soluble in water, and crystallizable; their solutions are colourless, while the air is excluded, but when it is admitted, they become turbid from decomposition; the oxygen of the air combining with the hydrogen, a portion of sulphur is deposited, and another portion, if the exposure be continued sufficiently long, combines with oxygen, forming sulphuric acid. They are decomposed by the acids, sulphuretted hydrogen being disengaged; and they preci-

pitate of a dark colour metallic solutions. They are also decomposed by heat, the sulphuretted hydrogen being partially expelled.

•HYDRO-SULPHURET OF POTASH, obtained by the above process, is in prismatic crystals, white and transparent; its taste is bitter and alkaline; it is inodorous when dry, but becomes fetid, if moistened. It attracts humidity from the air, is soluble both in water and alcohol, and when acted on by acids, gives out a considerable quantity of sulphuretted hydrogen.—HYDRO-SULPHURET OF SODA is also of a white colour, transparent, crystallized in tetrahedral prisms, acuminate by four planes. Its taste is at first acrid and alkaline, soon becoming extremely bitter: It dissolves abundantly in water, and produces cold in dissolving: its solution is colourless, but gives a green tinge to paper: it has a smell of sulphuretted hydrogen. Acids produce with it a brisk effervescence, and render this odour very strong; but they do not render the liquid turbid. The nitrous and oxy-muriatic acids, however, produce a precipitate of sulphur.—HYDRO-SULPHURET OF AMMONIA. This compound is formed by the direct combination of its principles in their aerial form, a thin soft deposit being formed on the sides of the vessel, which exhales a penetrating vapour when exposed to the air: by surrounding the vessel, during its formation, with a freezing mixture, it is obtained in white crystals. Another combination is obtained, by transmitting sulphuretted hydrogen through liquid ammonia, the liquid acquiring a yellowish green colour, and fetid odour. Another combination long known to chemists by the name of Fuming-Liquor of Boyle, is prepared, by exposing to heat in a retort a mixture of sulphur, lime, and muriate of ammonia; a liquor distils over of a yellow colour, which has a sharp fetid odour, and ex-

hales white vapours, when exposed to atmospheric air or oxygen gas. It varies considerably in the proportions of its constituent parts.

**HYDRO-SULPHURET OF BARYTES** is formed by transmitting sulphuretted hydrogen gas through water, in which barytes is suspended; it is abundantly soluble: when barytes and sulphur are boiled together in water, the barytes renders soluble about one-fourth of its weight of sulphur, and a solution is formed of a yellowish red colour, which, when concentrated, deposits crystals of the form of hexaedral prisms. These according to Berthollet consist of hydro-sulphuret of barytes, without any excess of sulphur. They give out, when acted on by an acid, a large quantity of sulphuretted hydrogen. They are white, transparent, and of a silky lustre. A similar result is obtained from either of these processes with Strontites; and it is probable that the compound is of the same nature. **HYDRO-SULPHURET OF LIME** can be formed by transmitting sulphuretted hydrogen gas through water in which lime is suspended. The compound is capable of crystallizing in prisms: it is soluble in water; the solution is without colour, but has a fetid smell. Sulphuretted hydrogen transmitted through water in which magnesia is suspended, dissolves a small quantity of it. Its relations to the other earths have not been examined.

**II. SUPER-SULPHURETTED HYDROGEN.**—Besides the compound of sulphur and hydrogen, which forms sulphuretted hydrogen, they combine in other proportions, so as to form different compounds. One of this kind formed by the action of alkaline sulphurets on water, was observed by Scheele, and afterwards by Berthollet. It has been

named Super-sulphuretted Hydrogen, and by some chemists Hydroguretted Sulphur. If a large quantity of muriatic acid be added to a solution of an alkaline sulphuret; or if small quantities of the solution be poured into the acid, a little sulphuretted hydrogen gas is disengaged, part of the sulphur is precipitated, but a portion exists combined with the remaining sulphuretted hydrogen, forming a liquid which has the appearance of oil, of a yellow or reddish colour, and which soon subsides to the bottom of the vessel. This is the Super-sulphuretted hydrogen.

It has been little examined in its insulated state, and is not easily submitted to chemical examination, as it is extremely susceptible of decomposition. Sulphuretted hydrogen escapes from it even at moderate temperatures, and it is decomposed by the action of the air. In its action, however, on the alkaline and earthy bases, it forms combinations of some interest and importance.

These compounds are obtained by boiling an alkaline or earthy hydro-sulphuret with an additional proportion of sulphur, or more simply by boiling sulphur with an earth or alkali in water, or by combining the sulphur with the earth or alkali by fusion, and then dissolving this in water. In either case, a decomposition of part of the water is produced; its oxygen is attracted by a portion of the sulphur, and sulphuric acid is formed, which is saturated by a part of the alkaline or earthy base. The hydrogen of the decomposed water unites with the remaining sulphur, and with it and the rest of the base forms a ternary compound soluble in water; and as there is in the liquor a great excess of sulphur, the combination established is not that which constitutes sulphuretted hydrogen, but is super-sulphuretted hydrogen. It is probable even that, according

to the relative proportions of the sulphur and alkali, these compounds may vary in the proportions of their constituent principles. They are of different shades of colour, from reddish yellow to a yellowish-green; and what is a proof of this diversity of proportion, they afford, when they are decomposed by an acid, variable quantities of sulphur by precipitation. The presence of the small portion of sulphate that is produced in their formation does not appear materially to modify their properties. They may be named, from the nature of their composition, Sulphuretted Hydro-sulphurets. They have been named Hydroguretted Sulphurets; but the name is so harsh that it can scarcely be adopted, and the other appellation, without being liable to this objection, very well expresses their constitution, and the difference between them and the hydro-sulphurets.

These liquors are transparent, of a yellow colour more or less deep, and of different tints. Their smell is fetid; they are immediately decomposed by the addition of an acid, which neutralizes the base, precipitates the greater part of the sulphur, and disengages the hydrogen combined with a portion of sulphur in the state of sulphuretted hydrogen: the quantity of this latter product is usually small. The precipitated sulphur is of a pale or white colour, either from its state of aggregation or combination with water.

The facility with which these compounds combine with oxygen forms their most important chemical property. If exposed, either to pure oxygen or to atmospheric air, the oxygen gas is absorbed, and the liquor continues to exert this action until nearly the whole of the sulphur is converted into sulphuric acid, and it becomes a solution of the sulphate of the alkali or earth with which the sulphur had

been combined. This facility of combination appears to be owing partly to the sulphur being in the liquid state, whence the resistance opposed by its cohesion in its usual form to its combination with oxygen does not operate; and partly to the alkaline or earthy base, by a resulting affinity promoting the combination of the sulphur and oxygen.

From this power of absorbing oxygen gas, these liquors have been applied to the purpose of endiometry, and they afford one of the best endiometers. The liquor employed is either the sulphuretted hydro-sulphuret of potash or of lime; the latter being easily prepared in a high state of concentration, is preferred. It is obtained by boiling equal weights of lime and sulphur in 10 or 12 times their weight of water. When a tube containing atmospheric air is placed in a portion of this liquor, the oxygen of the contained air is gradually absorbed, and the liquor rises within; and the tube being graduated, the quantity of oxygen abstracted is indicated.

This method of operating has the disadvantage of slowness; the liquor, from the smallness of the surface in contact with the air, absorbing the oxygen only gradually, and a considerable time being required to mark when the absorption has become complete. It is of importance, therefore, to accelerate the operation, and the apparatus which Dr Hope employs does so with every advantage. It consists (fig. 24.) of a small bottle designed to contain the sulphuretted solution; to the mouth of this a graduated tube is adapted by grinding, and towards the bottom of the bottle is an orifice fitted with a stopper. The bottle being filled with the solution, and its orifice being covered with a flat plate of glass, it is placed under the surface of water,

and the graduated tube containing the air subjected to trial, is inserted into it. The apparatus is removed from the water, is inclined so as to allow part of the liquor to flow into the tube, and agitated strongly. It is replaced in the water, and the stopper at the under orifice withdrawn, when, from the absorption of the oxygen of the air, a quantity of water rushes in. The stopper is again introduced, the agitation renewed, and the operation is repeated until the absorption proceeds no farther. The amount of this may be determined by plunging the bottle with the tube adapted to it into water, removing the stopper of the under orifice, and taking care that the water without is at the same level as the liquor within.

The diminution which atmospheric air suffers when subjected to this eudiometrical method, is between 21 and 22 in 100. Generally speaking, it is to be preferred to others, as of easy execution, and liable to few errors. The only fallacy to which it appears subject, is the absorption of a small quantity of nitrogen gas. If the liquor has been newly prepared by boiling, and used without previous exposure to the air, it will, in common with any other watery liquid, absorb a portion of the atmospheric air undecomposed, or of its nitrogen as well as of its oxygen, and the substances with which it is impregnated may even render the absorption of nitrogen greater than it would be by pure water: it has accordingly been found that nitrogen is absorbed by these liquids. This fallacy is obviated, by agitating the liquor, if it has been newly prepared, with atmospheric air before using it. It farther appears that when these liquors are kept for a considerable time in contact with the air, the condensed nitrogen combines with the hydrogen of the sulphuretted compound, and forms



ammonia ; a fresh portion of nitrogen is absorbed, and this continues to proceed, so that the diminution of volume is at length considerable ; Scheele, for example, having found it to amount in atmospheric air to 28 in 100 parts, undoubtedly from this cause. But, in performing the experiment in the above mode, this source of fallacy cannot operate.

The properties of the different compounds of super-sulphuretted hydrogen with the alkalis and alkaline earths are so similar as to require no distinct enumeration. They are all liable to vary in their state of concentration from the relative quantities of their ingredients. Those of potash, soda, ammonia, barytes, strontites and lime, may be obtained highly concentrated ; that with magnesia is less perfect, and contains much less sulphur dissolved.

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#### SECT. V.—Of Sulphuretted Carbon.

THE substance to which this name may be applied, was first observed to be produced by Lampadius, a German chemist, in submitting to heat a mixture of native sulphuret of iron with charcoal, or bituminated wood. The same, or a similar product, is obtained by exposing to heat a mixture of sulphur and charcoal, or passing sulphur in vapour over charcoal ignited in a tube. From its inflammability and volatility, he named it *Alkohol of Sulphur*. It affords a singular example of diversity of opinion with regard to the chemical constitution of a compound, even after repeated examination of it. Lampadius supposed it to be a compound of sulphur and hydrogen. Clement and

Desormes, on the contrary, observed that the charcoal disappeared in the process of its formation, if a sufficient quantity of sulphur were employed, and that in burning it gave a residuum of charcoal; hence they concluded, that it is a compound of sulphur and charcoal. The younger Berthollet, however, affirmed that it deposits no charcoal in its combustion, and that in the products no indication of carbonic acid could be discovered. Robiquet, assisted by Vauquelin, obtained the same results; and Sir H. Davy also drew the same conclusion from his experiments, and only found in it sometimes a minute quantity of charcoal. From all these it might be concluded, that this substance is a compound of sulphur and hydrogen. In opposition to this, however, are the other positive results; and from an examination of it more lately undertaken both by Thenard and by Berzelius and Marcet, it appears that it consists of sulphur and carbon alone,—a diversity of result proving probably that there are different compounds of this kind in which carbon and hydrogen may exist in combination with sulphur. According to Thenard, the proportions of its constituent parts, inferred from its decomposition by passing it slowly over copper in a red hot tube, are 85 of sulphur, and 15 of charcoal. The results obtained by Berzelius and Marcet, by decomposing it by passing it over oxide of iron at a red heat, give proportions almost the same, 84.83 of sulphur, and 15.17 of carbon.

This liquid when pure is colourless and transparent: has a penetrating odour and a pungent taste. It is highly volatile, and produces in its evaporation a great degree of cold; under the atmospheric pressure, the temperature falls from  $60^{\circ}$  to  $0$ , and in an exhausted receiver it falls to  $-80^{\circ}$ ; quicksilver therefore can be frozen by it; it boils

at 104 ; its specific gravity is 1300 ; it is sparingly soluble in water, and is more soluble in alcohol and ether. It is inflammable, and burns with a blue flame. When burnt in oxygen gas the principal product is sulphurous acid gas ; when this is removed, a mixture remains of carbonic acid and carbonic oxide gases ; and there is no trace of hydrogen or of moisture. This substance combines with alkaline bases, at least with ammonia and lime, forming compounds which Berzelius has named Carbo-sulphurets.

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SECT. VI.—*Of the Compounds of Sulphur with the Alkalis and Earths.*

SULPHUR combines with the fixed alkalis, and with several of the earths, forming sulphurets. These compounds are formed by exposing the alkali or earth, with the due proportion of sulphur, to a moderate heat in a covered crucible. They exist only in the solid form ; for when dissolved in water new combinations are established from the decomposition of the water, as has been explained under the preceding sections.

SULPHURET OF POTASH is formed by exposing to heat in a covered crucible, equal parts of sulphur and dry concrete potash ; the compound melts. When it has become concrete, it is firm and brittle, of a reddish-brown colour. A similar combination is obtained, by exposing to heat one part of sulphur with two parts of sub-carbonate of potash, but it appears to be less intimate : its colour is grey or green. Sulphuret of potash is inodorous while dry ;

but when moistened or dissolved, acquires a fetid smell, from the production of sulphuretted hydrogen. It is fusible, and when exposed to a strong heat in close vessels, a portion of sulphur is sublimed from it. From suffering decomposition when in a state of solution, it is scarcely possible to discover precisely its peculiar agencies.

SULPHURET OF SODA is formed by the same process as sulphuret of potash, and is similar in appearance.—SULPHURET OF AMMONIA does not exist, as there is no mode of bringing its elements to act on each other, without the production of sulphuretted hydrogen.—SULPHURET OF BARYTES is formed by exposing sulphur and barytes to a red heat in a covered crucible; the compound has a reddish-yellow colour.—SULPHURET OF STRONTITES is formed by a similar process, as is also the SULPHURET OF LIME; in external appearance they are nearly the same.

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SULPHUR is capable of combining with the bases of the alkalis and earths. Mr Davy found that it unites with potassium when they are brought into contact in tubes filled with the vapour of naphtha; there is a rapid evolution of heat and light, and a grey substance in appearance like artificial sulphuret of iron is formed. This sulphuretted potassium easily inflames; it is also oxygenated from exposure to the air, and converted into sulphate of potash. Sodium and sulphur combine with equal facility, intense heat and light being disengaged. The compound is of a deep grey colour. The phenomena displayed in these combinations are similar to those which attend the combinations of sulphur with the metals; and the compounds have properties similar to the metallic sulphurets.

## CHAP. III.

OF CARBONIC ACID, ITS BASE AND THEIR  
COMBINATIONS.

IN the combustion of charcoal an acid is produced which exists in the aerial form. Charcoal being a heterogeneous substance, or containing with its inflammable matter small portions of saline and earthy substances, the term Carbon was introduced to denote its pure base, and the acid formed in its combustion was hence named Carbonic Acid. Carbon, in this sense, therefore, denotes merely the inflammable matter of charcoal. It was afterwards discovered, that the same matter exists under other forms. The diamond, which was known to be combustible, was found by Lavoisier to yield carbonic acid as the only sensible product of its combustion, and hence came to be regarded as pure carbon. And the mineral substance known by the name of Plumbago or Graphite, was also found to be chiefly carbon with a small portion of iron. It is not certain but that charcoal, even in the purest state in which it can be prepared, contains hydrogen; and the existence of a minute portion of oxygen has been supposed in diamond, but this is doubtful. The term Carbon is understood to denote the pure inflammable base, of which these are different forms, and which, saturated with oxygen, forms carbonic acid. This element exists as a principal ingredient of all vegetable and animal substances, and is extensive.

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sively distributed in the mineral kingdom: Diamond, as its purest form, may first be considered.

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### SECT. I.—Of *Diamond*.

THE Diamond, the gem which, from its lustre and hardness, is of greatest value, is found in India and in Brazil. It occurs crystallized, is colourless or tinged of various shades, transparent, and has a laminated structure; in hardness it is superior to every other substance; its specific gravity is 3.5.

From its high refractive power, Newton conjectured that the diamond must be an inflammable body. It was found to be dissipated when placed in the focus of a powerful burning mirror, and even in the heat excited in a furnace. In the latter mode of making the experiment, its surface was observed to be luminous; and at length it was ascertained, that at a temperature sufficiently elevated it suffers a real combustion. Lavoisier, making experiments to ascertain the nature of the product of its combustion, observed, that if the diamond were not highly heated, its surface became covered with a thin coating of charcoal; and when by raising the heat higher, the combustion was rendered complete, the only sensible product was carbonic acid.

Mr Tennant, having burned the diamond by the aid of nitre in a gold tube, concluded from the product of carbonic acid, that the quantity afforded by a given weight of diamond is the same as is afforded by the same weight of charcoal, and hence inferred, that the diamond differs

from charcoal only in the state of aggregation and its crystallized form. Guyton advanced a different opinion. Having caused a fragment of diamond to burn in pure oxygen gas, by directing on its surface the solar rays concentrated by a lens, and estimating, at the end of the experiment, the quantity of carbonic acid it produced, he concluded that it exceeded considerably the quantity that would have been produced from the consumption of the same weight of charcoal, 100 parts of carbonic acid being obtained from the disappearance by combustion of 17.88 of diamond, while the same quantity is formed from the combustion of 28 of charcoal. He concluded, therefore, that the difference between these two substances is, that the diamond is the pure carbonaceous base, while charcoal contains oxygen, or is an oxide of carbon.

The mode, however, in which Guyton estimated the quantity of carbonic acid, was not free from objections; and more lately Messrs Allen and Pepys repeating the experiment of the combustion of the diamond and charcoal in oxygen gas, found that the proportions of oxygen consumed, and of carbonic acid formed from equal weights of each are the same; whence the conclusion follows, that they differ merely in aggregation and form. They differ so much in properties, that perhaps some doubt may still remain with regard to this conclusion; but if either of them contain any element producing a difference in chemical constitution, this seems not appreciable by experiment.

The diamond requires a high temperature to cause it to burn, and, even when kindled in oxygen gas, does not evolve so much caloric as to support the necessary heat. Its surface is blackened if the heat is not sufficiently high, and the illumination becomes brighter as it is raised.

The diamond is scarcely acted on by any other agent. By sulphuric acid heated on it, it appears to be charred; the other acids do not affect it, an inertness evidently owing to its state of aggregation. It is a non-conductor of electricity, a property in which it differs from charcoal.

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## SECT. II.—Of *Plumbago*, &c.

PLUMBAGO or Graphite is a mineral production. Its relation to carbonaceous matter, and at the same time the existence of iron in it, were first observed by Scheele; and from subsequent experiments by Pelletier and Monge, it was inferred to be a compound of carbon and iron, containing from 5 to 10 of iron in 100 parts, with which are also frequently mixed or combined portions of argil and silex. Guyton supposed, that it consumes more oxygen in its combustion than charcoal, and that, therefore, though an oxide of carbon, it approached nearer to the pure inflammable base. Messrs Allen and Pepys found, however, that the carbonaceous matter of it consumes the same quantity of oxygen, and affords the same quantity of carbonic acid as charcoal. Its carbonaceous base gives no indication of being combined with any portion of hydrogen. It so far approaches in chemical characters to the diamond as to be little acted on by any chemical agent, and to be so imperfectly combustible as to require a very elevated temperature, and the continued application of external heat to cause it to burn. As a compound of iron and carbon it is to be afterwards noticed.



The substance named Mineral Carbon, Incombustible Coal, or Anthracite, appears, so far as regards its carbonaceous matter, to be in a similar state. It differs from other coals in containing no bitumen; and it is less combustible, burning only at an elevated temperature, and scarcely evolving so much heat as is sufficient to sustain its combustion. With carbonaceous matter it contains portions of silex, argil, and iron. Guyton had supposed it to be an oxide of carbon at a lower degree of oxidation than common charcoal; but Allen and Pepys found that it consumes in burning the same quantity of oxygen, and affords the same quantity of carbonic acid; its inferior combustibility is probably owing to its state of aggregation.

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### SECT. III.—*Of Charcoal.*

CHARCOAL is obtained from the imperfect combustion of wood; the wood cut into billets being reared in a pile which is covered with earth or turf, apertures being left to regulate the circulation of air, by which the combustion, when the wood is kindled, is supported. This combustion is carried on as slowly as possible; the oxygen and hydrogen, with a portion of the carbon of the wood form elastic products, which are disengaged; and there remains the black porous substance which forms common charcoal, retaining frequently the figure and texture of the wood. To prepare it thoroughly, it requires to be exposed to a red heat with the exclusion of the air: this is done by covering it with sand. By the same method, well prepared charcoal may at once be obtained from wood, a

heat sufficiently intense having been applied. Charcoal is also deposited in the state of a fine powder, when alcohol or oil is transmitted through an ignited tube.

From the nature of the process, by which common charcoal is formed, it is obvious that there must exist in it any matter not volatile which entered into the composition of the wood; and accordingly it always contains portions of saline and earthy matter, chiefly carbonates of potash and lime, with a little oxide of iron. But these are present in comparatively minute quantities, and do not appear to modify its properties. Apart from these charcoal was regarded as pure carbon. Guyton, as has been already stated, supposed it to be an oxide of carbon; while Allen and Pepys, finding that it consumes the same quantity of oxygen, and forms the same quantity of carbonic acid, established the former opinion.

There are some facts, however, which support an opinion advanced by Berthollet, that charcoal contains hydrogen. It has been observed, that when charcoal is burnt in oxygen gas a sensible quantity of water is deposited; when it is urged with a strong red heat, a quantity of elastic fluid is given out, composed of carbon and hydrogen; and when heated with sulphur, sulphuretted hydrogen, or super-sulphuretted hydrogen is disengaged.

If charcoal is not thoroughly calcined, a portion of the hydrogen of the vegetable matter may no doubt exist in it. It appears too, that charcoal imbibes humidity very rapidly, absorbing it even from the air, and this may sometimes be the source of the hydrogen which appears. The question is, whether, independent of these sources of fallacy, there is any reason to conclude that hydrogen exists in charcoal; in other words, whether in perfectly calcined

charcoal any portion of this element can be detected. The determination is difficult. The fact that the quantity of elastic fluid containing hydrogen expelled from charcoal by heat, diminishes as the heat is raised, is favourable to the conclusion that it is not an essential ingredient, and that if the heat be raised sufficiently high it will be entirely expelled; and the result apparently established, that the same quantity of carbonic acid is produced in burning from well calcined charcoal as from diamond, and the same quantity of oxygen consumed, seems to prove that no hydrogen is present in the former. Still if the quantity of hydrogen is small, the water which it will form may exist in the elastic form combined with the carbonic acid, and add so far to its volume, as that this shall appear equal to the volume of carbonic acid produced from the combustion of the same weight of diamond, though this contain no hydrogen. Berthollet has affirmed, that when charcoal, which has been calcined by the most intense heat, is burnt in oxygen gas, or heated with oxide of mercury, a few drops of water appear at the beginning of the operation, which the carbonic acid gas afterwards dissolves. Calcined charcoal too, converts at first oxymuriatic gas into muriatic acid gas, a change which requires the presence of hydrogen. On continuing, however, the transmission of oxymuriatic gas, this effect ceases, and the charcoal in this state does not apparently acquire any new properties. The most probable conclusion, therefore, on the whole, is, that charcoal after exposure to an intense heat retains only a very minute portion of hydrogen, and that that element is not essential to its constitution.

Charcoal well prepared is brittle and porous, tasteless and inodorous. It is infusible in any heat a furnace can

raise; but by the intense heat of a very powerful galvanic apparatus, it is hardened, and at length is volatilized, but without any appearance of fusion. In its common state it gives out, when exposed in close vessels to a heat above redness, an elastic fluid, consisting principally of a variety of carburetted hydrogen: this diminishes as the heat is raised, and at length the production of it ceases. But even when it has been brought to this state, a portion of gas is expelled by the more intense heat which galvanism excites. This evolution of æriform matter is to be ascribed partly to the expulsion of hydrogen originally contained in the vegetable matter, from which the charcoal is prepared, and partly to the decomposition of water which the charcoal had imbibed, and accordingly part of it is carbonic acid, or carbonic oxide. These are more abundant in the first portions, a proof that the oxygen is more easily expelled than the hydrogen. By this high degree of calcination the charcoal is rendered a better electrical conductor.

Charcoal is insoluble in water, and is not affected by it at low temperatures. It absorbs a small portion of it, and hence, in cooling, it imbibes it from the atmosphere so as sensibly to increase in weight. At the temperature of ignition it decomposes water, the products being carbonic acid gas and a variety of carburetted hydrogen gas.

A singular property belonging to charcoal, is that of absorbing the different aerial fluids in considerable quantity without forming with them any intimate combination. If the charcoal, when ignited, is allowed to cool without exposure to the atmosphere, on exposing to it any gas the absorption takes place, and exceeds many times the volume of the charcoal. The extent of it is different with dif-

ferent aërial fluids : carbonic acid, muriatic acid, and ammonia, are largely absorbed, while oxygen, nitrogen, and hydrogen, are absorbed more sparingly. The condensed gas in general suffers no chemical change, and the greater part of it is again expelled by a heat inferior to that of boiling water, and also to a certain extent by immersion in water. Neither is there any apparent alteration in the properties of the charcoal. It is therefore a mechanical condensation, produced, probably, however, by a certain attraction exerted by the carbonaceous matter to the aërial fluid. In some cases, too, more intimate combination or decomposition takes place ; oxygen is converted into carbonic acid, and sulphuretted hydrogen, according to Thenard, deposits sulphur, the temperature becoming at the same time greatly elevated. Two gases thus condensed in the pores of the charcoal have also been found to combine ; oxygen and hydrogen when absorbed together, for example, forming water, and this being accompanied with a sensible elevation of temperature.

When the action of oxygen and of hydrogen gases is favoured by humidity, they appear to dissolve small portions of charcoal at common temperatures. At the temperature of ignition they form with it intimate combinations. In burning, charcoal combines with oxygen gas, forming carbonic acid : with a lower proportion of oxygen it forms carbonic oxide. If hydrogen gas be passed over charcoal in an ignited tube, an elastic fluid formed from their combination is obtained. Nitrogen does not unite with it. It forms combinations with sulphur, either alone or with hydrogen, as has been already noticed.

The alkalis scarcely sensibly dissolve charcoal when it is

pure, though in its common state they receive from it a dark brown colour. It decomposes a number of the acids by abstracting their oxygen, some suffering this decomposition at a low, others only at a high temperature.

One singular property, undoubtedly chemical, belonging to charcoal, remains to be stated: it is that of removing the odour, taste, and colour of a number of vegetable and animal substances, when triturated or digested with them by the medium of water. Thus, all saline substances, which, from the adherence of vegetable or animal extractive matter, are of a brown colour, may, after this process, be obtained white by a second crystallization. Resins, gum-resins, balsams, and essential oils, even those that have the strongest smell, are rendered nearly inodorous when they are rubbed with charcoal and water, or when solutions of them in alcohol are macerated with the charcoal, or filtrated repeatedly through it, and a number of the vegetable tinctures and infusions lose their colour, smell, and much of their taste, by the same process. It is from this agency that charcoal powder removes the offensive smell and taste which water acquires from keeping in wooden casks, and that it obviates even the putrescence of animal matter. To produce these effects, it is necessary that the charcoal should have been well calcined and newly prepared, or at least should not have been long exposed to the air. A certain quantity too is necessary, more or less, according to the effect required. It is not very obvious by what kind of agency the charcoal produces these effects.

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SECT. IV.—Of Carbonic Acid.

THIS is the Fixed Air of Dr Black, the first of the æri-form fluids which was submitted to accurate examination. He investigated a number of its properties, and the changes it produces in chemical combinations, particularly with the alkalis and earths. Bewly and Bergman discovered its acid powers, which, from being comparatively weak, had escaped Dr Black's observation.

Though this acid is produced without difficulty by the combination of its constituent principles, it is usually obtained by other processes. It exists, combined with lime, in the different varieties of limestone, marble, and chalk; if any of these be exposed to a strong red heat, the affinity of the acid to the lime is so far weakened, that it assumes the elastic form. Or, if the affinity of another acid to the lime is introduced, the same result is obtained without applying heat. Into a bottle fitted with a bent tube, small fragments of chalk or marble are put, and to this diluted muriatic acid is added; a strong effervescence is immediately excited from the disengagement of the carbonic acid gas, the muriatic acid combining with the lime: the gas may be collected over water, by which it is not immediately absorbed in any considerable quantity.

The experiment of the formation of this acid, by the combination of its principles, is of importance, as determining the proportions in which they are combined. Lavoisier, in performing this experiment by burning charcoal in oxygen gas, the charcoal having been previously

thoroughly ignited to avoid as much as possible any error from the production of water, fixed the proportions at a mean at 28 of charcoal and 72 of oxygen; and with this the results of the experiments of Clement and Desormes, and more lately of Allen and Pepys, exactly agree, the proportions assigned by both being 28.6 of carbon and 71.4 of oxygen. T. Saussure has fixed them at 27.11 and 72.89; and these agree with an estimate obtained in another way, founded on the fact, which is experimentally proved, that oxygen gas in combining with carbon suffers no change of volume, so that the increased density of the carbonic acid gas, or, in other words, the difference of specific gravity between it and the oxygen gas, shews the quantity of carbon with which the oxygen is combined.

The composition of carbonic acid has been established by its analysis. This is effected by a concurrence of affinities: a few pieces of phosphorus are put at the bottom of a coated glass tube, and over this is put a quantity of marble (carbonate of lime) in powder, or, what renders the experiment more easy of execution, carbonate of potash or soda dried. The part of the tube containing the carbonate is raised to a red heat; and the phosphorus being volatilized passes over the ignited carbonate, and decomposes the carbonic acid, by attracting its oxygen: phosphoric acid is thus formed, which unites with the alkali, and the carbonaceous base of the acid remains diffused through the mass in the state of charcoal. The decomposition is probably produced by the joint affinities of the phosphorus, and the alkaline or earthy base with which the carbonic acid is united to its oxygen, aided by the state of condensation of the acid, or to its being acted on in a nascent



state as disengaged by the heat. Potassium, from the strength of its affinity to oxygen, decomposes carbonic acid with facility, burning in the gas, and precipitating charcoal. And a partial abstraction of its oxygen is even effected by some of the metals, as iron or zinc, at a high temperature. Potassium in its action on the dry gas causes no evolution of hydrogen; and from this and some other facts, particularly its production by the combustion of dry charcoal in oxygen gas, carbonic acid has been inferred to contain no combined water: but the proofs of this are not altogether conclusive, and analogy would lead even to the opposite conclusion, though from its evident inferior attraction to water, the proportion may be comparatively small.

Carbonic acid has a considerable specific gravity: it is compared with atmospheric air as 1.519 to 1.000, or is one half heavier; 100 cubic inches weigh 47 grains; it is inodorous, has a pungent taste; it proves eminently fatal to life, an animal immersed in it being immediately killed; and even when diluted with two or three parts of atmospheric air, it exerts a deleterious power.

Carbonic acid in its elastic form is absorbed by water; the water, at a mean atmospheric pressure and temperature, absorbing nearly its own volume. The absorption is promoted by agitation; and the quantity absorbed is increased by cold, or by augmented pressure. The water, when largely impregnated with it, sparkles when shaken, and has a pungent taste; the gas escapes on exposure to the atmosphere: it is entirely expelled by boiling, and is disengaged by freezing.

The acidity of carbonic acid is weak. Its taste is scarcely perceptibly sour, either in its elastic or liquid form; it

reddens, however, the more delicate vegetable colours, as that of litmus; and though it adheres with little force to the bases with which it combines, this is owing in part to its greater tendency to pass into the elastic state; judging from its powers of saturation, it may even be regarded as superior in acidity to a number of the acids.

It combines with the alkalis, earths, and metallic oxides, forming salts denominated Carbonates. In these combinations with the alkalis, is displayed the peculiarity, that the alkaline properties are rather impaired than neutralized; it is at least difficult to establish neutralization, and the compounds, even when obtained of uniform composition by crystallization, retain to a certain extent the alkaline properties; they have the alkaline taste, change to a green the vegetable colours, and combine with oils so as to form soaps. The alkalis in this state were therefore formerly regarded not as existing in any state of combination, but were supposed to be in their purest form; they were named Mild Alkalis, to distinguish them from what were named Caustic Alkalis, which were supposed to be less pure. Dr Black shewed, that the mildness, as it was named, is owing to the presence of carbonic acid; and Bergman proved, that the mild alkalis are to be regarded as compound salts. They generally form, however, with an excess of base, and it is not very certain if they can be obtained otherwise, at least in a crystallized state. The property by which they are peculiarly distinguished, is that of effervescing strongly on the addition of any acid, the carbonic acid being disengaged, and assuming the elastic form. They are also easily decomposed, at least partially, by heat, the carbonic acid being expelled. In the earthy carbonates, however, it is retained with more force, and requires

a much higher heat. The law has been already stated which exists with regard to the relation between the carbonates and the sub-carbonates, that the proportion of acid in the former is just double of what it is in the latter. There is no sufficient reason to conclude, however, that the combination is restricted to these two proportions.

**SUB-CARBONATE OF POTASH.**—It is under the form of this salt that potash is afforded in the processes by which it is usually obtained, as in the incineration of the wood of plants. It therefore forms the base of the potash or pearl-ash of commerce, which also contains, however, other saline substances, particularly sulphate and muriate of potash, and earthy and metallic matter. From these it is in part freed, by dissolving the pearl-ash in an equal weight of warm water; the foreign substances being sparingly soluble, remain in a great measure undissolved; the clear liquor is poured off, and is evaporated until a pellicle appear on its surface; on cooling and remaining at rest for a few hours, it deposits a little muriate of potash, and being poured off from this and evaporated, the sub-carbonate is obtained. Other processes have been employed to procure it, such as burning tartar at a red heat: this substance consists of potash, combined with tartaric acid,—a vegetable acid having a compound base of carbon and hydrogen, and which, therefore, when decomposed by heat, affords carbonic acid, with which the potash combines. By deflagrating tartar with nitre, a similar product is formed, and also by deflagrating nitre with charcoal, the charcoal being converted into carbonic acid by the oxygen afforded by the decomposition of the nitric acid, and the carbonic acid combining with the potash, which is the base of the nitre. As obtained by these processes, the sub-carbonate

of potash is even purer than in the state in which it is procured from the pearl-ash of commerce.

Sub-carbonate of potash, obtained in a concrete state by evaporation, is in the form of coarse grains, as it is not susceptible of regular crystallization. From the excess of alkali it contains, it is deliquescent; if exposed to the air it soon attracts as much water as dissolves it. Its taste is acrid; it changes the vegetable colours to a green, and combines with oils, forming a saponaceous compound. It is decomposed by the acids; its carbonic acid being disengaged with effervescence. A considerable portion, but not the whole of its acid, is expelled by a strong red heat. It consists of about 60 of alkali, 28 or 30 of carbonic acid, and 6 of water, with a little siliceous earth, sulphate of potash, and argil.

CARBONATE OF POTASH may be obtained by exposing the solution of the sub-carbonate to the air for some time, carbonic acid being imbibed from the atmosphere, and crystals of the neutral carbonate being deposited. Or it is formed more directly by passing a current of carbonic acid gas through a solution of the sub-carbonate of such a strength that crystals form spontaneously. The crystals are bevelled quadrangular prisms; they do not, like the sub-carbonate, deliquesce. They require, at a mean temperature, four parts of water for their solution, and produce, while dissolving, a degree of cold. They are much more soluble in hot water, the water taking up even  $\frac{5}{8}$ ths of its weight; but if the temperature be that of boiling water, part of the carbonic acid assumes the elastic state, and rises through the liquor. The taste of this crystallized salt is more mild than that of the sub-carbonate, though still alkaline it has no causticity, but it unites with oils, and

changes the vegetable colours to a green : it can scarcely therefore be regarded as the neutral carbonate. It consists, according to its analysis by Pelletier, of 40 of potash, 43 of carbonic acid, and 17 of water. It is little used but for some medicinal purposes, but the sub-carbonate in the state of the potash and pearl-ash of commerce is applied to many uses in the arts, principally from the alkali it contains.

Potash is capable of combining with a less portion of carbonic acid, but still so as to form a crystallizable salt. It is also super-saturated by dissolving the sub-carbonate in water, (one ounce in ten pounds), and by the assistance of cold and pressure impregnating the solution strongly with carbonic acid gas ; the liquor, when a sufficient quantity of carbonic acid has been combined in it, is pleasantly acidulous, with some pungency, and the alkali thus super-saturated proves less irritating to the stomach than in any other state.

**CARBONATE OF SODA.**—The salt which usually receives this name is in strictness of nomenclature a sub-carbonate, for its taste is alkaline, and it changes the vegetable colours to a green. It is extracted from the saline matter obtained by the combustion of marine plants, the barilla of commerce ; the purer kinds of barilla being lixiviated with warm water, and the solution being evaporated, so that on cooling it shall crystallize. The crystals are octohedrons ; they are efflorescent, so as in a dry atmosphere to be soon reduced to a powder. They require, at a medium temperature, twice their weight of water for solution, and are more abundantly soluble in hot water, the saturated solution crystallizing on cooling. Exposed to heat, they suffer the watery fusion from the action of a large

quantity of water of crystallization; as this is dissipated, the salt appears as a dry white powder, which by an increase of heat may be fused and partially decomposed. The proportions of the crystallized salt are 21.58 of soda, 14.42 acid, and 64 water of crystallization. Soda saturated with carbonic acid may be obtained either by transmitting carbonic acid gas through a solution of the sub-carbonate, or, according to a process given in the London Pharmacopœia, mixing one part of it with three parts of sub-carbonate of ammonia, the carbonic acid of the latter salt being transferred to the soda, and the ammonia being distilled off. The residual liquor affords crystals of carbonate of soda. The alkali may also be super-saturated with carbonic acid by the same process as that followed with the carbonate of potash; and this super-saturated solution is like the other in medicinal use.

**CARBONATE OF AMMONIA.**—Ammonia, by combination with carbonic acid in different proportions, affords various products, in which, however, the alkali is not altogether neutralized. Though they exist in a concrete state, they are volatile, retain the pungent ammoniacal odour and taste, and change the vegetable colours to a green. The combination is easily established; by presenting the two gases to each other, they instantly unite and form a concrete salt: they unite in the proportions of 100 measures of the acid gas with 200 measures of ammoniacal gas, and the product of this combination is a sub-carbonate.

The process usually followed for its production is an indirect one, decomposing muriate of ammonia by carbonate of potash or lime. Equal parts of chalk, dried, and of muriate of ammonia, are mixed together, and put into an earthen retort, or an iron pot, to which a capital is adapted,

and which is connected with a large receiver. Heat is applied, by which a double decomposition is effected, the lime attracting the muriatic acid, and the ammonia, the carbonic acid. The muriate of lime remains in the vessel, and the carbonate of ammonia being volatilized, is condensed on the sides of the receiver in the form of a crust. Sometimes it is obtained by another process in solution in water. Equal parts of muriate of ammonia and of sub-carbonate of potash are put into a retort with two parts of water, and heat is applied; a double decomposition likewise takes place in this case, the muriatic acid uniting with the potash, and the carbonic acid with the ammonia; the carbonate of ammonia passes over with the aqueous vapour, which, when condensed, is sufficient to dissolve it.

Carbonate of ammonia is also obtained in large quantity in the decomposition of animal matter by heat. It is thus procured from bones, and forms the impure product which has been named salt of Hartshorn.

The composition of these products varies so much, that, according to their analysis by Davy, the quantity of ammonia is from 20 to 50 in 100 parts. The carbonic acid and water are super-abundant in it, as the temperature at which the compound has been formed is low; that formed at  $300^{\circ}$  contained, he found, above 50 of alkali, while that formed at  $60^{\circ}$  contained only 20; but in none of them is the alkali neutralized. The sub-carbonate, estimating its composition from its being formed of one measure of the one gas to two of the other, will consist of 44 of ammonia and 56 of acid by weight. Supposing the neutral carbonate to be formed from equal volumes, this would give the proportions of 28.2 of base and 71.8 of

acid : Berthollet, by analysis, found the proportions very near these, 26.7 of ammonia and 73.3 of acid.

Sub-carbonate of ammonia is very soluble in water ; at a mean temperature it requires only twice its weight, and at 212° less than its own weight is sufficient for its solution. Its saturated solution deposits crystals, the figure of which appears to be octohedral. Exposed to a very moderate heat, it is entirely volatilized, but is easily condensed, and its deposition on the sides of the vessel is of a regular dendritical form. It effloresces on exposure to the air, and its odour becomes weaker, from the loss of its moisture, or the absorption of carbonic acid.

This salt is used in medicine as a stimulant and diaphoretic, and as a stimulating perfume.

CARBONATE OF BARYTES exists native. When obtained by adding carbonic acid to barytic water, or by decomposing muriate of barytes by an alkaline carbonate, it is in the form of a white powder, of considerable specific gravity ; is not soluble in water in any appreciable quantity, but is dissolved in small quantity when the water is impregnated with carbonic acid. The native carbonate, and the artificial carbonate after it has been ignited, consist of 22 of acid and 78 barytes. The artificial carbonate is decomposed by heat, its carbonic acid being expelled ; while in the natural carbonate which contains less water, the decomposition is much more difficult : a difference owing to the water contained in the former, which by the affinity it exerts to the barytes, favours the separation of the carbonic acid. The same affinity favours even the expulsion of the carbonic acid by the action of another acid : When a little charcoal is added, the native carbonate is decomposed by



a red heat, by the carbonic acid being converted into carbonic oxide.

CARBONATE OF STRONTITES is precipitated, on adding carbonic acid, or a solution of an alkaline carbonate, to a solution of strontites, or of a strontitic salt. With an excess of acid it becomes soluble. The artificial carbonate, like that of barytes, is more easily decomposed than the native. The latter consists of 61.2 of strontites, 30.2 of acid, and 8.6 of water.

CARBONATE OF LIME exists in nature in great abundance and under a variety of forms, many of them regularly crystallized. It is formed by adding carbonic acid to lime-water, or by decomposing any of the soluble salts of lime by any of the alkaline carbonates. It is very sparingly soluble in water, and in those forms of it in which the cohesion is considerable, appears altogether insoluble. By an excess of carbonic acid, solubility is communicated. When exposed to heat, it first loses what water it contains, and, if transparent and hard, becomes white, opaque, and friable. If the heat be augmented, the carbonic acid is expelled, and pure lime remains. This operation is performed on a large scale, on the different varieties of the native carbonate, marble, chalk, and more particularly, limestone, to obtain lime for the numerous uses to which it is applied. The experiments of Sir James Hall have proved, that if the separation of the carbonic acid from its combination with the lime be prevented by the requisite pressure, the carbonate may be fused at a heat between 20° and 30 of Wedgwood's scale, according to the more or less perfect compression. A substance is thus formed, having considerable hardness and closeness of texture, and approaching by these qualities, as well as in fracture and spe-

cific gravity, to the finer kinds of limestone or marble. Bucholz has since discovered, that even without compression carbonate of lime is fused when it is submitted to heat in a large mass. The acids expel the carbonic acid from carbonate of lime, with effervescence; and this property of effervescing strongly on the contact of an acid, affords a discriminating character of carbonate of lime. The native carbonate perfectly pure, consists of 55 of lime, and 45 of acid.

CARBONATE OF MAGNESIA is prepared for medicinal use by dissolving equal weights of sulphate of magnesia and sub-carbonate of potash separately in twice their weight of water; mixing them together, and diluting with eight parts of warm water: the magnesia attracts the carbonic acid; and the compound being insoluble, is precipitated, while the sulphate of potash that is formed remains in solution. The mixture is made to boil for a few minutes: after cooling a little, it is poured upon a filtre: the clear fluid runs through, and the precipitate of carbonate of magnesia is washed with water till it is tasteless. When the process is conducted on the large scale, the bittern, or liquor remaining after the crystallization of sea salt, which is principally a solution of muriate and sulphate of magnesia, is substituted for the pure sulphate, and this is precipitated by a solution of pearl-ash, or of carbonate of ammonia procured by distillation from animal substances.

Carbonate of magnesia is perfectly white, nearly tasteless, possessing little coherence in its texture, and of a specific gravity not more than 2.3. It is very sparingly soluble in water; requiring at least 2000 times its weight, at the temperature of 60°. In this state, however, it is rather a sub-carbonate. When acted on by water impreg-

nated with carbonic acid, it is dissolved ; and from this solution allowed to evaporate spontaneously, the carbonate of magnesia is deposited in small prismatic crystals, which are transparent and efflorescent : they are soluble in 48 parts of water, at 60 ; and, by slow evaporation, this solution affords crystals. These consist of 25 of magnesia, 50 of acid, and 25 of water ; while the proportions of the common carbonate are, from 45 to 55 of earth, from 25 to 48 of acid, and from 15 to 30 of water.

CARBONATE OF ARGIL can scarcely be formed : water impregnated with carbonic acid dissolves a portion of the earth ; but in evaporating the solution, the carbonic acid is expelled ; and when an argillaceous salt is decomposed by an alkaline carbonate, the argil is precipitated, and retains little carbonic acid combined with it.

The other earthy carbonates are scarcely known. CARBONATE OF ZIRCON is insoluble. CARBONATE OF GLUCINE, obtained by double decomposition, is precipitated in a soft state, and is not easily dried ; is insipid, insoluble in water, and is not rendered soluble by an excess of acid.

Water impregnated with carbonic acid dissolves small portions of some of the metals, particularly iron and zinc. By indirect modes it can be combined with their oxides, forming compounds afterwards to be noticed.

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#### SECT. V.—Of Carbonic Oxide.

CHARCOAL, in burning, combines with that proportion of oxygen which converts it into carbonic acid. But an

intermediate product in the state of an oxide, can be obtained by processes in which oxygen and charcoal are combined in a different mode, or in which carbonic acid is decomposed and its oxygen partially abstracted.

The processes in which the production of carbonic oxide was first observed, consist in exposing mixtures of certain metallic oxides, particularly the grey oxide or scales of iron with charcoal to a red heat; a large quantity of elastic fluid is disengaged, which consists partly of carbonic acid; but when this is abstracted by agitation with water, there remains an elastic fluid inflammable, and which, in burning, is converted into carbonic acid; it has hence been regarded as a gaseous oxide of carbon. In its formation the oxygen of the metallic oxide combines with the charcoal, and from the excess of charcoal present, forms this oxide rather than carbonic acid.

There are other processes in which a similar product is obtained from the partial decomposition of carbonic acid. Thus, if native carbonate of barytes, or dried carbonate of lime, be mixed with zinc or iron filings, and exposed to a low red heat, there is an abundant production of elastic fluid; this contains a small portion of carbonic acid, but it consists principally of an inflammable gas, which, like the former, is converted into carbonic acid in burning, and towards the end of the process this gas is even disengaged perfectly pure. Its production must be ascribed to the metal abstracting a portion of the oxygen of the carbonic acid disengaged from the carbonate of barytes or carbonate of lime. And this decomposition, so as to afford this product, is established by another process still more direct,—passing carbonic acid gas repeatedly through an iron-tube, containing clean iron wire at a red heat; the iron is oxi-

dated, and the carbonic acid, if the process is continued sufficiently long, is converted into carbonic oxide.

Some chemists, Berthollet in particular, have supposed that this gas always contains a portion of hydrogen, and is therefore a ternary compound, not a pure carbonic oxide. When obtained from processes in which charcoal is employed, the hydrogen which this inflammable substance usually contains, may enter into combination with the oxygen and carbon which form the elastic product, and exist in it either as a constituent ingredient, or mixed with it in the state of carburetted hydrogen; and accordingly the gas produced by this process has been observed, in burning, not only to form carbonic acid, but to deposit also a portion of water. As obtained, however, by other processes, there is no deposition of water; and its production from the decomposition of the carbonic acid existing in carbonate of barytes, a compound in which carbonic acid appears to exist without even that small portion of water which the acid contains in its usual form, as well as its production from carbonic acid gas, which has been previously exposed to the action of muriate of lime, so as to abstract any water, render more probable the conclusion that hydrogen is not essential to the constitution of this elastic fluid, or at least prove that the quantity of that element in its composition must be extremely small. It is therefore the most probable opinion, that it is an oxide of carbon. There is one fact, indeed, rather singular with regard to this gas, which is favourable to the supposition that hydrogen is one of its elements,—its comparative levity. It is rather lighter than atmospheric air: oxygen gas is heavier: when combined with carbon, a heavier ingredient, it might, in retaining the elastic form, be ex-

pected still to become specifically heavier, and it actually does so in forming carbonic acid; yet, in increasing the proportion of carbon farther so as to form carbonic oxide, it becomes specifically lighter. And though some attempts have been made to account for this, it is still not very satisfactorily explained.

Carbonic oxide is permanently elastic. Its specific gravity is to that of atmospheric air as 957 to 1000. 100 cubic inches weigh 29 grains. It is absorbed in small quantity by water, 100 cubic inches condensing 2 of the gas: it has no acid taste, nor either in this condensed state or in its elastic form does it contract any union with the alkalis or earths. It burns with a blue lambent flame, but does not explode when previously mixed with atmospheric air and kindled; and it is necessary to its complete combustion, that an excess of oxygen should be present: 100 cubic inches of it consume, according to Cruickshank, 40, according to Dalton 47, and according to Gay-Lussac 50 cubic inches of oxygen gas. It forms a quantity of carbonic acid gas equal in weight to the carbonic oxide and oxygen consumed. From the products Cruickshank inferred that it consists of 21 of oxygen and 8.6 of carbon. Clement and Desormes state them at 58.4 of oxygen and 41.6 of carbon. If the estimate of Gay-Lussac, that 100 measures of the carbonic oxide combine with 50 of oxygen, and form 100 measures of carbonic acid gas, be correct, it follows, as 100 measures of carbonic acid gas contain exactly 100 measures of oxygen gas, that carbonic oxide contains just half the quantity of oxygen that carbonic acid contains, or that 100 measures of it contain 50 measures of oxygen. Reducing these proportions to weight,

they give, as the composition of carbonic oxide, 43 of carbon and 57 of oxygen.

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SECT. VI.—*Of Carburetted and Oxy-carburetted Hydrogen Gases.*

THERE are obtained, in different processes, inflammable elastic fluids, which, in their combustion, afford carbonic acid and water in different proportions, and which are, therefore, compounds of carbon and hydrogen, or of carbon, hydrogen, and oxygen, and as such may have the common name of carburetted hydrogen or oxy-carburetted hydrogen applied to them. There is much difficulty in determining their composition, and there is even some uncertainty with regard to their specific distinctions,—whether some of them are not mixtures of others. Two opinions are at present maintained with regard to them; one admits the existence of only two species, both compounds of carbon and hydrogen in definite proportions, which may hence be denominated carburetted and super-carburetted hydrogen gases, and supposes all the others to be mixtures of these with hydrogen and carbonic oxide; the other opinion rests on the conclusion, that carbon, hydrogen, and oxygen combine in numerous, perhaps in indefinite proportions, and that the various elastic fluids obtained by these processes are the products of combinations of this kind. The specific distinctions and properties of those which are best defined may first be stated, and these opinions may then be considered.

A gas arises from marshes produced by the decomposition of vegetable matter, which is inflammable, and yields water and carbonic acid in its combustion. It has been examined by Mr Dalton and Dr Thomson, who have both considered it as a binary compound of carbon and hydrogen, and as the gas to which the name of Carburetted Hydrogen ought to be appropriated. It is always mixed with nitrogen gas and carbonic acid gas, but when these are abstracted it is of uniform properties. Its specific gravity is 0.555 : 100 cubic inches weigh 17 grains ; water absorbs  $\frac{1}{7}$  of its volume of it. It burns with a yellow flame ; it explodes but feebly when mixed with atmospheric air ; and when mixed with oxygen gas, it is necessary that the oxygen should be considerably in excess ; 100 measures consume 205 measures of oxygen, and form 104 measures of carbonic acid gas. Carbonic acid gas contains its own volume of oxygen ; hence 100 measures of the oxygen consumed are inferred to combine with the hydrogen of the gas to form water ; this gives the proportions of 72 of carbon and 28 of hydrogen, as entering into its composition. This gas may likewise be analysed by the action of oxy-muriatic acid gas. When they are exposed over water to light, oxygen is transferred from the oxymuriatic acid, and the whole mixture being converted into carbonic and muriatic acids is absorbed by the water.

The other inflammable gas, which is regarded as a binary compound of carbon and hydrogen, is that which has been known by the name of Olefiant Gas, and which it is now proposed to name Super-carburetted hydrogen, as containing a larger proportion of carbon than the former. It is formed during the latter stage of the process of the for-



mation of what is named Sulphuric Ether, by the action of sulphuric acid on alkohol at a high temperature; or it can be obtained directly by mixing three parts of sulphuric acid by weight with one part of alkohol, and submitting the mixture in a retort to a moderate heat. The elastic fluid disengaged is the olefiant gas mixed with a portion of sulphurous acid gas; the latter is abstracted by agitation with water, and the former remains pure. It derives the name by which it is distinguished, from a singular chemical property it exhibits, that, when mixed with oxymuriatic acid gas, condensation of the two gases quickly takes place, and a liquid is produced from their action, which collects in a film on the surface of the water, and afterwards into globules having all the appearance of oil; it is rather heavier than water, and hence the globules soon sink; it is whitish and semi-transparent, has a smell somewhat aromatic and a sweetish taste. By agitation with water it is dissolved: alkohol and ether also dissolve it, sulphuric acid disengages a smell of oxymuriatic acid, and nitrate of silver forms a precipitate of muriate of silver. The theory of its production is not very well ascertained; but it appears to contain muriatic or oxymuriatic acid in combination with carbon and hydrogen.

Olefiant gas has a specific gravity very nearly the same as atmospheric air, the difference being only as 974 to 1000. It has an odour slightly fetid; is absorbed in small quantity by water; it is decomposed by transmission through an ignited tube, depositing charcoal; and charcoal is also precipitated from it by the agency of the electric spark, while it is converted into a lighter inflammable gas, without any deposition of moisture or production of carbonic acid. It appears, therefore, to contain no oxygen. It

burns with a dense oily flame, and the emission of much light; and if previously mixed with a sufficient quantity of atmospheric air or oxygen gas, detonates with the utmost violence. Of any of these inflammable gases, it is the one which consumes the largest quantity of oxygen in its combustion, and gives the largest product of carbonic acid; and from its greater specific gravity compared with the other inflammable gases, it is evident that its principles are in a state of greater condensation. There is considerable diversity of result in the experiments of different chemists, with regard to the quantity of oxygen which it consumes, and the quantity of carbonic acid it forms. Hence the estimate of its composition is various. Berthollet has stated it at 75 of carbon, and 25 of hydrogen. Dr Thomson at 80 and 20, and T. Saussure at 86 and 14.

Besides these two well defined species, there are a number of gases containing carbon and hydrogen produced in different processes; and their composition is so liable to be diversified by slight variations in the circumstances of their production, that it is not easy to arrange them with precision. Those which are best characterized may be noticed.

A gas is formed, which is nearly pure olefiant gas, by passing the vapour of alkohol either over ignited siliceous or argillaceous earth. From the gas which is disengaged in the decomposition of wood, and of some inflammable vegetable products by heat, burning with a dense oily flame, it might be concluded to be analogous; but it is much lighter, and consumes in burning a much smaller quantity of oxygen. The gas disengaged from the bituminous matter of coal by heat, and which has been applied to the purpose of affording illumination by its combustion, is of a si-

nular nature. It burns with a dense oily-like flame, even when it has been freed by washing from the bituminous matter suspended in it; and it consumes in burning, as Dr Henry has found, a larger quantity of oxygen gas, and affords a larger product of carbonic acid. It appears, however, not to be the same with the olefiant gas. It varies, too, as obtained from different kinds of coal; and there are some varieties of it which are lighter than any other species of carburetted hydrogen, the specific gravity being so low as 900, and even 190; air being 1000. Besides these, there are a number of other inflammable gases, containing chiefly carbon and hydrogen disengaged in different processes, or from different substances decomposed by heat, which differ from each other in specific gravity, and in the quantity of oxygen they consume, and of carbonic acid which they form. Thus, if oil or wax be decomposed by a red heat, a gas is produced, which, like the olefiant gas, burns with much illumination, but is of so low a specific gravity as 0.348. While 100 measures of olefiant gas consume in burning 284 measures or more of oxygen gas, the gas from wax consumes only 220, that from oil 190. Another is obtained by passing the vapour of camphor through a red hot tube, 100 measures of which in burning consume 176 measures of oxygen. The vapour of alkohol or of ether submitted to the same experiment, yields gases which are lighter, combine with less oxygen, and afford less carbonic acid.

Lastly, a gas known formerly to chemists by the name of Heavy Inflammable Air, is produced from humid charcoal, or the vapour of water passed slowly over charcoal at a red heat, inferior to all these in the quantity of oxygen which it consumes in burning, and the quantity of carbo-

nic acid which it yields. In the process in which it is formed, a quantity of carbonic acid is also formed by the oxygen of the water decomposed combining with the charcoal; this is abstracted by washing with water, and the inflammable gas remains. Its specific gravity compared with air is 0.555: it burns with a weak lambent flame. 100 measures of it combine in burning with 66 measures of oxygen, and produce 40 of carbonic acid gas, with 9 grains of water deposited. It is extremely deleterious in its action on the living system when received into the lungs. An animal breathing it pure is almost instantly killed; and even when diluted with 20 parts of atmospheric air, it produces, when respired, sickness, vertigo, fainting, and other symptoms of exhausted power. It has the peculiar effect on the blood of giving to it a florid red hue.

The products of the combustion of these gases are carbonic acid and water: they contain therefore carbon and hydrogen. But when the quantity of oxygen which they consume is compared with the quantity of carbonic acid and water which they afford, the consumption of oxygen is less than the quantity which enters into the composition of these products; hence it follows, that they must contain oxygen either in direct combination with the carbon and hydrogen, or combined in a binary combination, mixed with carburetted hydrogen. The gas from humid charcoal contains, for example, according to Berthollet, 38.6 of oxygen in 100 parts, with 44 of carbon, and 22.4 of hydrogen; that from camphor contains 25.35 of oxygen, with 48.69 of carbon, and 26.02 of hydrogen; and there are other proportions with regard to the others.

Two opinions I have stated are maintained with regard to this. Mr Dalton, Dr Henry and other chemists, sup-

pose: that these gases are mixtures of one or both of the species of carburetted hydrogen, the gas from marshes and the olefiant gas with carbonic oxide gas, and hydrogen gas. It has appeared to me more probable, that the carbon, hydrogen and oxygen are in direct combination, forming what may properly be named Oxy-carburetted Hydrogen Gases; and this opinion is supported by Berthollet. There may sometimes be an intermixture, particularly of carbonic oxide, but it is mere hypothesis that this is always the case. It is still more an assumption altogether gratuitous and extremely improbable, that these gases have an intermixture of pure hydrogen; for in all the processes in which they are produced, carbon is presented to this element under the circumstances under which they combine. And the intermixture of olefiant gas appears to be precluded with regard to the greater number of them, by the circumstance that it is actually decomposed at a red heat. On the other hand, when it is considered that carbon, hydrogen, and oxygen have strong mutual affinities to each other, it is sufficiently probable *a priori*, that these affinities may be so balanced as to admit of their union in simultaneous combination in various, perhaps in indefinite proportions, so as to give rise to the numerous elastic fluids which are formed by slight diversities in the processes above described; a probability, confirmed by the fact that these elements exist in such combinations in the immense diversity of organic products.

Besides the analysis of these gases by combustion, it may be stated, in concluding their history, that they are all decomposed by the operation of another powerful chemical agent,—oxy-muriatic acid gas. If mixed with them over

water and exposed to light, condensation speedily takes place, and the whole is converted into water, carbonic acid, and muriatic acid: the oxy-muriatic acid affording oxygen to the hydrogen and carbon of the inflammable gas. A similar action is exerted, accompanied with detonation, when the electric spark is transmitted through the mixture of these gases. From some of them, especially the olefiant gas, part of the carbon is precipitated in the state of charcoal. Carbonic oxide does not detonate with oxy-muriatic acid gas, and this, independent of other characters, discriminates it from these gases.

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## CHAP. IV.

### OF PHOSPHORIC ACID, ITS BASE, AND THEIR COMBINATIONS.

**P**HOSPHORIC acid, by decomposition, affords Phosphorus, a substance distinguished by its high inflammability; it is the base of this acid, forming it by combination with oxygen. With a smaller proportion of oxygen, it forms Phosphorous Acid. With hydrogen it produces an elastic compound. It unites with sulphur and the metals, and is acted on by the alkalis and earths. It must, in the present state of our knowledge with regard to it, be considered as a simple substance; for though some results were at one period obtained from the action of galvanism, and also from the action of potassium upon it, whence it was inferred to contain small portions of oxygen and hydrogen; it now appears that these were inaccurate, and there is no fact whence its compound nature can be inferred.

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#### SECT. I.—Of *Phosphorus*.

It was known to some of the alchemists, that a substance might be procured which burns spontaneously on

exposure to the air. Kunckel made known the process by which they obtained it, that of distilling urine to dryness, and urging the residuum with a strong heat; the phosphoric acid existing in the salts of the urine is decomposed, and its oxygen abstracted by the animal matter. By the addition of charcoal, this decomposition is facilitated: and the product is also increased, by adding a portion of muriate of lead, which, abstracting the phosphoric acid from the soda and lime with which it is in part combined, allows it to be more easily decomposed.

This process, however, is offensive and difficult, and phosphorus is now obtained with more facility, by decomposing phosphoric acid in a purer form. Scheele discovered, that the solid matter of bones, obtained by burning them to whiteness, is a compound of phosphoric acid and lime. This reduced to powder is submitted to the action of half its weight of sulphuric acid, diluted with from 10 to 20 parts of water, aiding their mutual action by the application of a moderate heat. The sulphuric acid exerts an affinity to the lime, and combines with a portion of it; the phosphoric acid, holding the remaining lime in combination, is obtained by lixiviating the materials with boiling water; the solution of super-phosphate of lime thus procured, is evaporated to dryness; the dry mass is mixed with half its weight of charcoal powder, and the mixture is urged with a fire gradually raised in an earthen retort with a wide neck, to which a copper tube is adapted, the extremity of which dips in water; the charcoal attracts the oxygen of the phosphoric acid, and the phosphorus is volatilized and condenses, partly in the tube and partly in the water. The process, from the great inflammability of the product, requires considerable care. The phosphorus



has a brown colour, from the presence of a small quantity of carbonaceous matter, which is removed by straining it through leather when melted under warm water; or by digesting it with a little nitric or oxymuriatic acid. When melted under water it is run into moulds, so as to be formed into cylindrical pieces.

Phosphorus, when pure, is nearly colourless, and is semi-transparent. It has the consistence of wax, with rather more brittleness. Its fracture is often radiated, shewing a crystalline structure, and by slow cooling it can even be crystallized in octohedrons. It melts at  $99^{\circ}$  of Fahrenheit; is volatilized at  $219^{\circ}$ , and boils at  $564^{\circ}$ .

Exposed to atmospheric air it emits white fumes; and in the dark appears luminous, the light arising from its combustion, and the white vapours from the product combining with the water of the atmosphere. If heated to  $400$  the illumination is brighter; and at  $160$  it burns with the emission of much heat and light. Its rapid combustion is also excited by friction without heat. In oxygen gas its combustion is vivid, and the heat and light intense. A fact rather singular is, that the slow combustion at low temperatures does not take place in oxygen gas as it does in atmospheric air; the heat requires to be raised to above  $80$ , and below  $60$ , the phosphorus, if the oxygen is pure, has not in the dark any luminous appearance. From the experiments made to determine the cause of this peculiarity, it appears, that the slow combustion of phosphorus in atmospheric air is an indirect process; the phosphorus is dissolved in small quantity by the nitrogen gas, and in this state being presented to the oxygen, combines with it: hydrogen gas has the same property of dissolving it, and hence a little nitrogen or hydrogen, added to oxygen gas,

in which phosphorus is placed, causes the luminous appearance from the slow combustion.

The slow combustion of phosphorus in atmospheric air affords a simple eudiometrical process. The air measured in a tube, divided into 100 equal parts, is transferred into another tube, rather larger, in which it is exposed to the action of a cylinder of phosphorus, supported on a glass rod; the oxygen gradually combines with the phosphorus, and the product is absorbed by the water over which the air is confined. The diminution of volume is ascertained at the end of the experiment, by transferring the air into the graduated tube. This method is easy in the execution; the result is obtained in a few hours; and it has the advantage of indicating when the process is complete, the rise of white vapours from the phosphorus and its luminous appearance in the dark continuing while any oxygen is present, and ceasing when the whole has been abstracted. It requires only one correction; the nitrogen gas dissolving a small portion of phosphorus, receives from this an increase of volume, and hence the diminution with this method is not so great as with some of the others. The increase amounts to about a fortieth; hence, if the residual gas, when the experiment has been made on atmospheric air, be equal to 80 parts, indicating an abstraction of oxygen equal to 20, the quantity really abstracted is equal to 22.

Phosphorus is oxygenated by other substances. It burns in oxy-muriatic acid gas, in nitric oxide gas, and in nitrous acid vapour, and receives oxygen from nitrous acid.

When saturated with oxygen, it forms a concrete acid, the Phosphoric. When the oxygenation is less perfect, what is named Phosphorous Acid is produced. The ex-

istence of an oxide of phosphorus has also been supposed. A reddish coloured substance, which is left in its imperfect combustion, has been considered as such; but this is not certain, nor is the existence of any well defined oxide of phosphorus clearly established. Of these two acids there is reason to believe that the one contains double the quantity of oxygen of the other.

Phosphorus forms with hydrogen an elastic compound, highly inflammable. Its compounds with sulphur in different proportions are likewise more inflammable than pure phosphorus. With charcoal it appears to form an imperfect combination. It unites with the greater number of the metals, and forms compounds retaining to a certain extent metallic lustre. The alkalis and alkaline earths act upon it, and enable it to decompose water, whence phosphuretted hydrogen is produced.

Inflammable liquids, as alcohol, ether, and the oils, either expressed or volatile, dissolve phosphorus, especially when their action is aided by a moderate heat. The solutions in oils are luminous when exposed to the air, with scarcely any sensible heat. The solution in alcohol gives a vivid momentary illumination when dropped on water, and the phosphorus is precipitated from it.

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### SECT. II.—Of *Phosphoric Acid*.

PHOSPHORIC acid is obtained by the rapid combustion of Phosphorus in oxygen gas: it is a flocculent substance of a white colour, which deliquesces on exposure to the air.

The phosphorus, in burning, absorbs its own weight and a half of oxygen; the acid, therefore, consists of 40 of phosphorus, and 60 of oxygen.

Phosphoric acid is obtained most economically from the decomposition of the phosphate of lime of calcined bone, by sulphuric acid, by the process already described. To the solution of super-phosphate of lime, carbonate of ammonia is added, the ammonia of which combines with the phosphoric acid, forming phosphate of ammonia, which remains in solution, while the carbonate of lime, formed by the union of the carbonic acid with the lime, is precipitated: the phosphate of ammonia is procured solid by evaporation, and being exposed to a red heat, the ammonia is expelled, and the acid is fused. It is liable to retain a minute portion of lime. It is therefore best obtained in a state of purity by the oxygenation of phosphorus. This is done either by the action of nitric acid, or by exposing sticks of phosphorus to the air, in a wide vessel, in which the vapours of the phosphorous acid, formed by the spontaneous combustion of the phosphorus, are condensed. A small portion of nitric acid is added to the liquid to complete the oxygenation; the water is evaporated, and, by raising the heat, the phosphoric acid may be fused.

Phosphoric acid, obtained by the combustion of phosphorus, is a white spongy substance, which may be melted by heat, but is not volatile: it attracts moisture from the air, and it dissolves in water, producing heat. The water combined with it cannot again be expelled from it by heat, but even after fusion and ignition it remains to the amount of nearly one-fourth of the weight. In this state it may be named hydro-phosphoric acid: it forms a transparent glass; is deliquescent, and very soluble in water.

Phosphoric acid has a high degree of acidity. Its affinities to the alkalis and earths are strong; and it exceeds the other acids, with the exception of the fluoric, in the power of neutralizing the alkaline properties. It does not act forcibly on the metals or inflammables, owing to the strength of affinity with which the oxygen is retained in combination with its base; but it combines with the metallic oxides. Its salts are named phosphates. The alkaline phosphates are soluble and crystallizable, and melt into a glass. The earthy phosphates are insoluble.

PHOSPHATE OF POTASH can scarcely be crystallized, but forms a gelatinous mass, which attracts humidity from the atmosphere; its taste is saline, with a degree of sweetness. Exposed to heat, it liquefies, and, after the expulsion of the water, is fused by a red heat into a glass.

PHOSPHATE OF SODA, a salt employed in medicine, is prepared, by adding to the acidulous phosphate of lime, obtained from the decomposition of burnt bones by sulphuric acid, as much of a solution of carbonate of soda as may be sufficient to saturate the phosphoric acid; phosphate of lime is precipitated, and the water holding dissolved the phosphate of soda, is separated by filtration; by evaporation the salt is crystallized, its formation in regular crystals being promoted by a slight excess of alkali. The form of the crystals is a rhomboidal prism. They effloresce on exposure to the air, are soluble in three parts of cold water, and in half that quantity of boiling water. The taste of this salt being purely saline, without bitterness, it has been introduced into the practice of medicine as a substitute for other aperient salts. As it melts easily, and promotes the fusion of the earths and metallic oxides, it is used as a flux, in analyses performed by the blow-pipe.

PHOSPHATE OF AMMONIA is soluble in four parts of water at the temperature of 60°; it crystallizes in prisms, which are neither efflorescent nor deliquescent. By exposure to heat, it is fused into a transparent glass, and decomposed, part of its ammonia being expelled. Heated with charcoal, its acid suffers decomposition, its oxygen being abstracted, which is not the case with the other phosphates. Like phosphate of soda, it may be used with advantage in analyses by the blow-pipe.

PHOSPHATE OF BARYTES is an insipid white powder, of considerable specific gravity: it is insoluble in water; is fusible at a high temperature; and is not decomposed by exposure to heat mixed with carbonaceous matter.

PHOSPHATE OF STRONTITES, when perfectly neutral, is very sparingly soluble in water, requiring about 2000 parts for its solution. It melts into an enamel by the flame of the blow-pipe; giving a phosphorescent light.

PHOSPHATE OF LIME, formed by decomposing the solution of an alkaline phosphate by muriate of lime, is in the state of a white powder, insoluble, and which is imperfectly vitrified by a very intense heat. It exists in the mineral kingdom under different forms, some of them crystallized; and it is the base of calcined bone. When partially decomposed by an acid, it is converted into a super-phosphate, which is soluble, and, by evaporation of its solution, crystallizes in silky fibres or in brilliant scales, which, by heat, are fused into a transparent glass.

PHOSPHATE OF MAGNESIA, formed from the combination of the acid and the earth, crystallizes in prisms which are efflorescent, soluble in about 50 parts of cold water, and in a smaller quantity of boiling water, and which by heat melts into a glass. PHOSPHATE OF ARGIL forms an

insipid powder: it melts before the flame of the blow-pipe into a transparent globule. PHOSPHATE OF ZIRCON is insoluble. PHOSPHATE OF GLUCINE is in the form of a white powder, or of a viscous substance, insipid, and insoluble in water, but rendered soluble by an excess of acid. It is melted by heat into a transparent vitreous globule. PHOSPHATE OF LITHEA, formed by complex affinity, is insoluble, being thrown down in a gelatinous precipitate.

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### SECT. III.—*Of Phosphorous Acid.*

This acid is formed in the slow combustion of phosphorus in atmospheric air. It constitutes the base of the white vapour which arises from the surface of the phosphorus, and which appears to be composed of it with water which it attracts from the atmosphere; it condenses and forms a dense liquor, which has a smell slightly fetid, and a taste extremely sour. This is a mixture of phosphorous and phosphoric acids. When exposed to heat, part of the water is volatilized; and as this proceeds, a vapour is formed, probably phosphorus in solution in watery vapour, which, disengaged at the surface, affords a dense white smoke, attended with a luminous appearance, visible in the dark, and, by continuing the heat until this ceases, the phosphorous acid is deprived of its peculiar smell, and is converted into phosphoric acid. From this experiment, some chemists have considered phosphorous acid as phosphoric acid, holding a portion of phosphorus dissolved. This opinion, however, does not appear to be

just. There seems to be a definite compound of phosphorus and oxygen forming phosphoreous acid. According to Sir H. Davy, it is obtained solid by burning phosphorus in a very rare air; it is volatile at a moderate heat. It is calculated to consist of 57.2 of phosphorus and 42.8 of oxygen. Combined with water, it forms what may be named Hydre-phosphorous Acid, which, when fused, appears as a white crystalline solid. In this state it is best obtained by subliming phosphorus through corrosive sublimate of mercury, adding water to the product, and evaporating to a thick consistence.

Phosphorous acid unites with the alkalis and earths, forming salts named Phosphites. These, in several of their properties, resemble the phosphates. They are distinguished from them by appearing luminous when heated by the blow-pipe, and by affording, by distillation, a small quantity of phosphorus. They detonate with oxy-muriate of potash, and precipitate gold from its solution, in a metallic state. They pass very slowly into phosphates from exposure to the air. Those formed from the alkalis are soluble and crystallizable; those from the earths are insoluble, but acquire solubility from an excess of acid. They are so unimportant as not to require farther notice.

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#### SECT. IV.—Of Phosphuretted Hydrogen.

THIS compound of phosphorus and hydrogen exists in the elastic form. It is obtained by combining phosphorus with any substance which, by a resulting affinity, shall



enable it to decompose water. Thus, if one part of phosphorus is heated with 10 or 12 parts of a solution of potash, the alkali exerts this operation, one portion of the phosphorus combines with oxygen from the decomposition of the water, and forms phosphoric acid, with which the potash combines; another portion of the phosphorus is dissolved by the hydrogen of the decomposed water, and the elastic compound is disengaged. Another process is to combine phosphorus with dry lime, by causing the phosphorus to pass in vapour over lime included in a tube, which is raised to a red heat. This phosphuret of lime dropt into water instantly decomposes it, and phosphuretted hydrogen rises in the gaseous form, the lime favouring the action of the phosphorus on the water, as the potash does in the other process.

The distinguishing property of this gas is its high inflammability, in consequence of which it takes fire when it is presented to the atmospheric air. It cannot, with safety, be mixed with this air, even in small quantities; it is therefore merely allowed to burn as it escapes from the water in which the extremity of the retort containing the materials producing it is immersed. Presented in single bubbles to oxygen gas, its combustion is still more violent, and is accompanied with intense light. The products of the combustion are phosphorous acid and watery vapour, and a singular appearance is presented by these: the bubble of gas, as it escapes and inflames, expands into a horizontal ring of light white vapour, which enlarges in diameter as it rises, until it breaks; this is phosphorous acid wafted by the watery vapour, and it owes this form to the eccentric impulse of the explosion.

This gas is permanently elastic; it is sparingly soluble

in water; its smell is fetid, very similar to that of putrid animal matter, though more faint. It has no sensible acidity. By remaining over water it is decomposed. From the products of its combustion, it is obvious that it is a compound of phosphorus and hydrogen. Its elements appear, too, to combine in different proportions, for it varies in specific gravity as much as from 0.435 to 0.852, and the gas disengaged at the commencement of the process by which it is usually obtained, is not so highly inflammable as that which is afterwards formed. Sir H. Davy has described another compound of phosphorus and hydrogen, obtained when the solid product of the action of oxymuriatic gas on phosphorus is mixed with water, and decomposed by heat: a portion of the oxygen of the water converts the phosphorous acid of the product into phosphoric acid; and the hydrogen dissolving a portion of phosphorus, forms a gas which is not spontaneously inflammable, but detonates when mixed with atmospheric air, and heated to  $212^{\circ}$ . Its smell is unpleasant, but not so fetid as that of phosphuretted hydrogen; its specific gravity is 0.87. It is stated to consist of 4.5 of hydrogen, and 22.5 of phosphorus. He names it Hydro-phosphoric Gas.

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#### SECT. V.—Of Phosphuretted Sulphur.

SULPHUR and phosphorus combine by the application of heat, the mixture of them being usually heated under water to avoid the combustion of the phosphorus, and even the experiment in this way requires to be conducted with caution, and on small quantities. The compound is more

feasible than the phosphorus alone ; its fusibility is greatest when it is formed from about equal parts, the mass remaining liquid at temperatures above  $60^{\circ}$  ; in other proportions it is solid but soft. In its formation a portion of water appears to be decomposed ; and when the heat is raised a little high, phosphuretted hydrogen is disengaged, and sometimes so rapidly as to produce an explosion. A portion of oxygen therefore probably exists in the composition of the compound. Dr Briggs gave a process in which the sulphur and phosphorus are combined in the dry way : heat being applied to them in a tube firmly corked by plunging it in warm water, and raising the heat gradually until the water boil. He has observed, that this compound is different from that formed under water. When a small proportion of sulphur has been used, it is solid when cold, and has a crystallized appearance ; the other is spongy and friable. The former is less inflammable than the latter, but is rendered equally inflammable by kindling it in the tube with a hot wire, and allowing it to burn for a few seconds, oxygen probably being communicated to it from the air, or from the water formed by the combustion. Both are more inflammable than phosphorus, and hence these compounds are employed in forming the phosphoric match bottles ; a very small proportion, however, of sulphur being added to the phosphorus, as with too large a quantity the compound is soft.

## CHAP. V.

## OF BORACIC ACID, ITS BASE AND COMBINATIONS.

THE salt named Borax has long been known in commerce, and applied to some uses in the arts. It is a native production brought from Thibet in an unrefined state, and consists of soda combined with a peculiar acid, which has derived from it the name of Boracic Acid. The acid is procured either by dissolving the borax in warm water, and adding sulphuric acid, which combines with the soda, the solution on cooling depositing the acid in soft scales, which are freed from any adhering sulphuric acid or sulphate of soda by a second crystallization; or adding to sulphuric acid, diluted with an equal weight of water, two parts of borax in powder, and applying a moderate heat; the sulphuric acid combines with the soda, the boracic acid is volatilized by its affinity to the watery vapour, and condenses in scales in the neck of the retort.

Boracic acid submitted to the action of galvanism or of potassium, undergoes decomposition. The effect is best obtained with potassium. Equal weights of dry boracic acid and potassium are exposed to a red heat in a glass or copper tube; the mixture at the heat of  $300^{\circ}$  becomes ignited, a small quantity of hydrogen gas is disengaged, probably from the decomposition of a little water in the acid; part of the acid is decomposed, the potassium is converted into potash, and a substance of a dark grey colour remains

mixed with potash and borate of potash; these are abstracted by the action of water, and the coloured substance remains undissolved. Gay-Lussac and Thenard described its principal properties. When dried it forms a powder of a greenish brown colour, which is insipid: it is neither fused nor volatilized by heat, but, as Davy has stated, becomes more dense: it is insoluble in water or in alcohol, neither does it decompose water: it is not acted on by oxygen at a common temperature; but when raised to a red heat, it burns in atmospheric air, and more vividly in oxygen gas: the product of the combustion is boracic acid: it is oxygenated by nitric acid, and also when heat is applied, by sulphuric acid, and it takes oxygen from a number of compound salts and of metallic oxides.

There can be little doubt that this substance is the base of boracic acid, or at least it stands in the same relation to that acid that sulphur does to sulphuric acid, or carbon to carbonic acid. Sir H. Davy has given it the name of Boran. From its oxygenation by nitric acid, Gay-Lussac and Thenard inferred, that the boracic acid contains one-third of its weight of oxygen combined with this base. Sir H. Davy supposes the acid does not contain much less than two-thirds of its weight of oxygen.

Boracic acid is in the form of white brilliant scales, soft to the touch; these appear to consist of the real acid in combination with water; the quantity of water, according to Sir H. Davy, is about 0.43; its taste is bitterish, with a slight degree of sourness; it reddens the vegetable colours. It is not altered by exposure to the air; is soluble in 20 parts of cold water, and in 5 of boiling water. It is also soluble in alcohol, and, what is a distinctive character of it, gives to the flame of alcohol in burning a green colour.

Exposed to heat the hydrated acid swells and yields wa-

ter; when the heat is raised to redness, it is fused into a glass, which is soluble again in water. By the most intense heat it is not volatilized; but if water be present, the aqueous vapour elevates with it a portion of the acid.

Boracic acid combines with the alkalis and several of the earths, forming compounds named Borates. These retain the property of communicating a green colour to the flame of alcohol. They are decomposed by all the acids, the carbonic excepted, in the humid way; but in the dry way, the boracic acid, from its great fixity, is able at a high temperature to decompose those salts, the acid of which has a tendency to assume the gaseous form. The alkaline borates are soluble in water, the earthy are the reverse.

BORATE OF POTASH, like the other borates, has a tendency to form with an excess of alkali; it is soluble in water; by slow evaporation its solution affords prismatic crystals, which are not changed by exposure to the air. It is fused into a glass by heat.

BORATE, or rather SUB-BORATE OF SODA, the Borax of Commerce, is a native production, being obtained from a lake in Thibet, from the sides of which it is dug up, and where there appears to be a constant reproduction of it. In the state in which it is imported, it is impure, but is purified by calcination, solution and crystallization. In the state in which it is met with in the shops, it is in the form of crystalline masses, of a figure irregular, but approaching to an hexaedral prism. It is not perfectly neutral, but contains an excess of soda, which seems necessary to cause it to crystallize, the solution of the neutral salt forming by evaporation a gelatinous mass: it is soluble in 12 parts of cold, and in 6 parts of boiling water; it is very slightly efflorescent; when exposed to a moderate heat, it melts from the water of crystallization it contains; when this is eva-

porated, there remains a spongy white mass, named Calcin'd Borax. If the heat be raised to ignition, this is melted into a pellucid glass which suffers no decomposition. It is decomposed by the greater number of the acids and by potash and the earths, the former uniting with its alkali, the latter with its acid. From the facility with which it melts and brings other substances into fusion, it is of use in some arts, as in making of glass, especially the finer glass for imitating the gems, in assaying minerals by the blowpipe, and in soldering the more valuable metals.

BORATE OF AMMONIA, though little known, has been described as being obtained by evaporation of its solution in prismatic crystals, of a sharp taste, and which change the vegetable colours to a green, evidently, therefore, containing an excess of alkali.

BORATE OF BARYTES.—This compound, formed by adding boracic acid to barytic water, is precipitated in the form of a white powder, insipid, and insoluble.—BORATE OF STRONTITES forms a similar precipitate, which dissolves in 130 parts of boiling water.—BORATE OF LIME is precipitated in the state of an insoluble powder, white and insipid.—BORATE OF MAGNESIA is obtained by evaporation, in a crystalline mass, of no regular form. With the addition of lime, it forms a mineral substance, known by the name of Boracite. It occurs crystallized, in cubes, which are so hard as to scratch glass; semi-transparent; of a white colour, with a shining lustre.—BORATE OF ARGIL is obtained by evaporation of its solution, in the form of a viscid substance, through which minute crystals are interspersed, having a very astringent state.

Boracic acid acts very feebly on the metals, but may be combined with their oxides by complex affinity.

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CHAP. VI.OF MURIATIC ACID, OXYMURIATIC ACID, AND  
THEIR COMBINATIONS.

FROM Sea Salt, an acid is procured by distillation with sulphuric acid, formerly known to chemists by the name of Spirit of Salt, now named Muriatic Acid. It exists as a permanent gas, but is condensed by water in very large quantity, and forms a liquid acid of considerable strength.

This acid had always resisted the usual methods of chemical analysis. The evolution of hydrogen in its action on metals, and the production of a certain quantity of the same element by the action of the electric spark, had led some chemists to conclude that hydrogen is its base; but these facts were considered as more satisfactorily accounted for from the decomposition of water combined with the acid. This water, however, had been supposed to be inconsiderable in quantity, and not of much importance in its relation to the acid. To Gay-Lussac and Thenard we owe the discovery, that it amounts to nearly one-fourth of the weight of the acid in its gaseous state, that it is combined with it by a powerful attraction, and that without this combined water the acid cannot exist in an insulated form.

While these chemists drew these conclusions from their experiments, they observed, that a different hypothesis might be advanced, on which the results could be explain-



ed. This they did not defend, but it has since been maintained by Sir H. Davy; and before proceeding to the history of the acid, it will be necessary to give a brief view of the opinions which are thus at present held with regard to its chemical constitution.

When muriatic acid is distilled from substances which impart oxygen readily, as from black oxide of manganese, it is converted into what has been named Oxymuriatic Acid, a substance which exists in the gaseous form, and is distinguished by very peculiar properties. The manganese losing a quantity of oxygen in this experiment, the muriatic acid, it was inferred, combines with this oxygen, and the oxymuriatic acid is the product of this combination, a conclusion which appeared to be confirmed by the fact, that when oxymuriatic acid condensed by water is exposed to the rays of the sun, oxygen gas is given out, the oxymuriatic acid disappears, and muriatic acid remains combined with the water. Both analysis and synthesis appeared thus to concur in proving, that oxymuriatic acid is a compound of muriatic acid and oxygen.

Gay-Lussac and Thenard found, that when equal volumes of oxymuriatic gas and hydrogen gas are mixed and exposed to light, they act chemically, and are converted with little or no condensation into muriatic acid gas. If oxymuriatic acid be a compound of muriatic acid and oxygen, this result must be considered as arising from this oxygen combining with the hydrogen gas, and forming water, which the muriatic acid retains in combination with it in the gaseous form; and from the quantity of hydrogen which thus disappears, it must be inferred, that the quantity of water formed is equal to 0.25 of the weight of the muriatic acid gas. They accordingly found, that

when muriatic acid gas is presented to substances with which acids combine, and when the product is one having no great attraction to water, a quantity equal to this is rendered sensible, — muriatic acid gas, for example, yielding, when transmitted over oxide of silver or oxide of lead, 0.25 of its weight of water : or, when the acid gas acts on metals which, when aided by the resulting affinity of an acid decompose water, hydrogen gas is evolved in a proportion equal to what would be afforded by this quantity. These facts appeared to prove, that oxymuriatic acid is a compound of real muriatic acid with oxygen, and that muriatic acid gas consists of this real acid with one-fourth of the weight of the gas of combined water.

These chemists farther shewed, that the acid cannot be obtained in an insulated state without this water. From compounds in which it exists, from dry muriate of potash, or of soda, for example, it cannot be expelled by the most intense heat, aided even by the affinity of another acid to the base, unless this acid contains water, or unless a little water be added; but if this be done, the disengagement of muriatic acid gas quickly takes place. And for the same reason, oxygen cannot be abstracted from oxymuriatic acid unless either water be afforded to admit of the transition of its muriatic acid to an insulated state, or unless the substance exerting an attraction to its oxygen form an oxidated product, which exerts an affinity to muriatic acid, and with which the real acid combines. Hence the real acid is not in any case obtained, but is always either separated in combination with water, or enters into a new combination.

All these phenomena may, however, be explained in a different manner. Since muriatic acid gas is the only

sensible product of the mutual action of hydrogen and oxymuriatic gases, it may be inferred, that muriatic acid is a compound of these, and that their mutual action is a case of simple combination. The deposition of water which occurs when muriatic acid gas is presented to salifiable bases, — metallic oxides, for example, may be the consequence of the decomposition of the acid, its hydrogen uniting with the oxygen of the oxide, and forming this water, while the other element of the acid, the oxymuriatic principle, combines with the metal. The evolution of hydrogen which attends its action on metals may, in like manner, be owing to its decomposition, the oxymuriatic element combining with the metal, and the hydrogen becoming insulated. The agency of water, in favouring the evolution of muriatic acid from all these compounds, may be that of causing the reproduction of the acid, the hydrogen of the water combining with the oxymuriatic acid, while its oxygen unites with the metallic base. And the production of oxymuriatic gas in distilling muriatic acid from substances which impart oxygen, may be owing to the oxygen combining with the hydrogen of the acid forming water, while the oxymuriatic gas is liberated. Thus all these facts may be explained on this view of the constitution of muriatic and oxymuriatic acids; and no oxygen being capable of being abstracted from oxymuriatic acid, unless water be present which may afford it, there is no evidence, it is contended, that oxymuriatic gas is a compound, but, on the contrary, the most strict inference is, that it is a simple body. Sir H. Davy, regarding it as such, considers it as an element belonging to the same class as oxygen, forming like it by combination with inflammables and metals, compounds analogous either to

acids or oxides; and as in this view the term oxymuriatic acid would be improperly applied to it, he has given it, (from one of its most characteristic properties, its yellowish green colour,) the name of Chlorine.

It is not easy to give a distinct and condensed view of a subject so complicated, but I shall endeavour to state the question in the simplest form, without entering on details inconsistent with the plan of an elementary work.

The leading fact is, that when oxymuriatic gas and hydrogen gas are submitted to mutual action, muriatic acid gas is the only sensible product. Did we know nothing of the constitution of muriatic acid gas, the direct conclusion from this experiment would be, that it is a case of simple combination, and that, therefore, muriatic acid is a compound of these two gases. But before drawing such a conclusion, it is necessary, if we are to guard against the error of hasty generalization, to inquire whether muriatic acid gas is real muriatic acid or not. If it is, the inference is just; if it is not, some other conclusion must be drawn.

When we submit muriatic acid gas to the action of substances with which acids in general combine, and by which they are neutralized, (alkalis for example, earths or metallic oxides), there is this apparent neutralization, and at the same time a quantity of water is obtained. The most simple and direct conclusion here is, that the acid and the base have combined together, and that the water obtained above that which the base may have contained, has been derived from the muriatic acid gas,—that muriatic acid gas, therefore, is not the real acid, but contains a portion of combined water.

Is this evidence of the existence of water in muriatic acid gas conclusive? All that can be said in reply to this is, that it

is the same as that by which the existence of combined water in other acids is proved: the phenomena in both cases are precisely alike,—the apparent neutralization of the acid and of the base, the formation of a product having saline properties, and the production of a quantity of water. If we add sulphuric acid to oxide of lead, there will be the neutralization of the acid, the formation of a compound of sparing solubility, and a portion of water will be obtained. If nitric acid vapour be transmitted over potash, there will be the mutual neutralization of the acid and alkali, the production of a saline compound from which water can be expelled by heat, exceeding in quantity the water which the potash contained. We consider the proof from these facts as conclusive, that combined water has existed in these acids. But the phenomena from the action of muriatic acid gas on oxide of lead, or on potash, are exactly the same, and might be justly stated in the very same terms. The induction equally follows, therefore, that it contains combined water, and rests on evidence the same as that which is admitted to be conclusive with regard to the others.

The only peculiarity with regard to muriatic acid is one of little importance,—that of its existence in combination with water, in the gaseous form, at natural temperatures. It is obvious that this makes no essential distinction. Temperature is merely relative, and *a priori* it is just as probable that a compound of an acid with water should be gaseous as that it should be liquid or solid. Yet it is very probable, that the not attending to this obvious conclusion has been the cause of any difficulty being supposed to be attached to the admission, that muriatic acid contains combined water, and that had this acid, like the sulphuric or nitric, been liquid at natural temperatures, the infe-

rence would have been admitted with regard to it, with as much facility as a similar inference with regard to these acids.

The nature of muriatic acid gas being thus ascertained, and the existence of combined water in it being established, we are enabled to draw the just conclusion with regard to its production from the mutual action of oxymuriatic and hydrogen gases. No other conclusion can be drawn, than that the oxymuriatic acid gas is a compound of muriatic acid and oxygen, and that its oxygen enters into union with the hydrogen, forming the water which the acid holds combined with it in the gaseous form.

The principal conclusion being thus established, it is scarcely necessary, in this general view, to prosecute the discussion in its more minute details. It is enough to remark, (as I have I trust sufficiently shewn at the commencement of the controversy on this question; Nicholson's Journal, vol. 28, &c.) that no evidence more conclusive has been brought forward in support of the new hypothesis, and that its explanations are more complicated, and more at variance with analogy than those of the opposite opinion.

What assumption can be more gratuitous than that when muriatic acid is presented to a metallic oxide, both the oxide and the acid are decomposed, the oxygen of the one uniting with the hydrogen of the other to form water, while the chlorine and the metal combine? Or what conclusion more direct and simple, or more conformable to analogy, than that the acid and the oxide enter into combination, producing mutual neutralization, and liberating any combined water which the acid may have contained?

What inference can be more probable *a priori* than that

muriatic acid should contain combined water? All the other powerful acids do so, and its affinity to water does not seem to be less strong than theirs. Or what conclusion can be less conformable to analogy, than that it alone of all the powerful acids should exist altogether free from water in an insulated state?

The substances which muriatic acid forms when it acts on the alkalis, earths, and metallic oxides have all the properties of neutral salts. Many of them have the saline taste, are abundantly soluble in water, crystallizable, some are deliquescent, others efflorescent, and in no respect do they differ in general properties from other saline compounds. Yet we are to believe, on the new hypothesis, that they are not of a saline nature, but consisting of chlorine and metals, are rather similar to metallic oxides.

Lastly, there is no fact which the common doctrine does not explain. Much stress indeed was laid by Sir H. Davy on the circumstance which he states first led him to doubt of the existence of oxygen in oxymuriatic acid,—that charcoal, a substance having so powerful an attraction to oxygen, occasions no abstraction of that element, nor any change whatever in oxymuriatic gas, even when aided by the most intense heat. Nothing is more easy than to assign the cause of this. To admit of the transition of oxymuriatic acid to the state of muriatic acid, a portion of water, essential to the existence of the latter in an insulated state, must be supplied: this the charcoal cannot yield. Whatever therefore may be the strength of attraction which it exerts to oxygen, muriatic acid gas cannot be formed; and as the product of the oxygenation of charcoal is not a substance exerting affinities to acids, the muriatic acid cannot in this, as in the case of the action of

metals on oxymuriatic gas, pass into a state of new combination. The actual result is therefore precisely what is to be looked for,—the oxymuriatic gas suffers no change. But on the opposite hypothesis, if chlorine be an element like oxygen, exerting affinities to inflammable bodies, and combining with them, why should it not combine with charcoal?

It is unnecessary to add to these illustrations. They are sufficient to shew, in the present state of the investigation, the superiority of the common doctrine in the evidence on which its principles rest, their conformity to the strictest analogies, and their adaptation to the phenomena.

The opposite opinion, however, though so far inferior, and resting as a *theory* on vague views of what constitutes chemical induction, is still a possible *hypothesis*, which may be maintained. It were desirable, therefore, to obtain evidence of such a nature as to establish the one to the exclusion of the other. With this view, I have made a number of experiments, of which, however, I can give only the most general notice.

The question may be decided either by proving the existence of oxygen in oxymuriatic gas, or the existence of water in muriatic acid gas. In one series of experiments directed to the former of these objects, carbonic oxide was submitted to the action of oxymuriatic acid gas with a portion of hydrogen gas, the latter being added with the view, that by forming a certain portion of water with the oxygen of the oxymuriatic acid, it might favour so far the transition to the state of muriatic acid, and favour therefore the farther communication of oxygen to the carbonic oxide, so as to convert it into carbonic acid. The result was the production of a portion of carbonic acid,—a result incon-



sistent with the new hypothesis, since according to it there is no source whence oxygen could be communicated. In another series of experiments, the object was to gain proof of the existence of water in muriatic acid gas, from results which could not be otherwise explained. The production of water when the acid is combined with any oxidated base, as the fixed alkalis, the earths, or the metallic oxides, is so far liable to ambiguity that it can be accounted for on the new doctrine, by supposing the water to be formed by the oxygen of the base combining with the hydrogen assumed to exist in the acid. But there is one substance which may be employed free from this ambiguity,—ammonia; it contains no oxygen, and if water be obtained when muriatic acid gas is combined with it, there is no mode of accounting for it, but by the conclusion that it is derived from the muriatic acid gas. On making the experiment, with the necessary precautions to exclude extraneous moisture, water was obtained. The quantity was indeed inferior to that which may be obtained from combinations of the acid in which the product is insoluble, and fixed, for the volatility of the ammoniacal salt, and the attractive force with which water is retained in it, counteract the separation, while in compounds having no apparent attraction to water, and to which from their fixity a high degree of heat can be applied, the separation can be rendered much more complete. But still the obtaining any water is a conclusive result, since according to the new hypothesis, none whatever ought to be obtained.

The results in both these series of experiments were at first denied. It was affirmed, that the carbonic oxide remains unchanged, and that no carbonic acid is obtained; but the reverse of this was afterwards admitted, and at-

tempted to be accounted for, by the supposed operation of a new gas, a compound of oxymuriatic gas and carbonic oxide, which, decomposing water, forms muriatic and carbonic acids. The ammoniacal muriate does not yield, it was asserted, the most minute trace of water, unless it has been previously exposed to the atmosphere, from which it was supposed to imbibe moisture. But it was afterwards admitted, that water is produced in minute quantity even when the air has been excluded; and I subsequently found, that exposure to the air has no influence on its production, that the salt absorbs no water from the air in a common state of dryness, and that water is obtained when the air has been entirely excluded. The experiment therefore remained equally conclusive. To enter on any farther details with regard to these results, would be however incompatible with the limits of this elementary view.

It may be concluded, on all these grounds, that the common doctrine with regard to the relation between muriatic and oxymuriatic acids is just. Oxymuriatic acid is a compound of muriatic acid and oxygen. The composition of muriatic acid is still unknown to us, and the acid itself, like sulphuric or nitric acid, is even unknown in its pure state, being obtained only in combination with water. Muriatic acid gas is therefore hydro-muriatic acid.

MURIATIC ACID is always obtained from sea-salt decomposed by sulphuric acid, one part of the acid being added to two parts of the salt. The sulphuric acid combines with the soda, which is the base of the salt; and the muriatic acid, which is the other ingredient, is disengaged, and assumes the elastic form. The gas may be received over quick-silver, as it is rapidly absorbed by water; or if it is to be procured liquid, the retort containing the materials is con-

nected with the bottles of Woolfe's apparatus, in which water is placed, by which its condensation is effected, a moderate heat being applied, by the medium of a sand-bath, as long as any acid is produced. The process is facilitated by diluting a little the sulphuric acid.

Muriatic acid gas, when free from watery vapour, is transparent and colourless; it is pungent and suffocating; its specific gravity is, to that of air, as 1278 to 1000; 100 cubic inches weigh 38 or 39 grains. The acid in this state contains, as has been already stated, about 0.25 of its weight of combined water.

Water instantly condenses muriatic acid gas in large quantity, absorbing nearly 500 times its volume of the gas, by which its weight is doubled: this absorption is attended with a rise of temperature. In the liquid muriatic acid obtained by the usual process of distillation, the water is not saturated with the gas; its specific gravity seldom exceeds 1.170, and the strongest that can be easily procured is that of 1.196: when of this strength, it contains, according to Kirwan's estimate, 25 of acid. The liquid acid in its common state has a yellow tinge; but this arises from impurity, and by distilling it from a little muriate of soda, it is obtained colourless. It emits white vapours, having a pungent smell, and, even when largely diluted, has a very sour taste, and reddens the vegetable colours.

As muriatic acid does not directly communicate oxygen, it does not act with much energy on inflammable substances; and it dissolves metals only by enabling them, by the resulting affinity it exerts, to decompose water and attract its oxygen; hence these solutions are attended with a disengagement of hydrogen gas. It combines with all the metallic oxides; it also unites easily with the alkalis and

earths. Its salts are named Muriates; the alkaline and earthy muriates are soluble and crystallizable, and have in general that taste peculiarly denominated saline. According to the new hypothesis, the greater number of these substances, as well as of the metallic muriates, are compounds of chlorine with metallic bases.

MURIATE OF POTASH has a taste saline and slightly bitter; it is soluble in three parts of cold, and in half its weight of boiling water, the latter solution crystallizing on cooling; its crystals have a cubic form, they are slightly deliquescent, and decrepitate when heated. It consists of 64 of potash and 56 of acid.

MURIATE OF SODA is the salt which exists in largest quantity in nature. It is the principal saline ingredient of the ocean, forming what is named Sea Salt, and it exists in immense beds in the earth forming Rock Salt. In the latter, it is nearly pure; in the former it is less so, a portion of other salts adhering to it, greater or less according to the method in which it is procured. In warm climates, it is obtained by spontaneous evaporation, the sea-water being admitted into shallow trenches by the sea-side, and spread over an extensive surface: as it becomes concentrated by the evaporation of the water, the liquor is removed, by sluices, from one trench to another, until at length the muriate of soda crystallizes spontaneously, and with scarcely any intermixture of the other salts. In colder climates, the sea-water is evaporated in large boilers by the application of heat, and the evaporation is carried so far, that the salt concretes in small crystals on the surface of the boiling liquor: As obtained by this mode, small portions of muriate and sulphate of magnesia adhere to it, which render it slightly deliquescent, and somewhat impair its antiseptic power.

Muriate of soda crystallizes by slow evaporation in cubes; it has a saline taste with scarcely any bitterness; is soluble in less than three parts of cold water, and its solubility is very little increased by raising the temperature even to  $212^{\circ}$ ; hence it crystallizes from its solution, not by cooling, but by slow evaporation. Its crystals neither deliquesce nor effloresce; they decrepitate when suddenly exposed to heat, the water of crystallization being dissipated in vapour; the salt melts at a red heat, and at a more intense heat is volatilized. It consists, when freed from water, of 45 of acid and 55 of base.

Muriate of soda is in common use to counteract the process of putrefaction in animal matter, and the theory of its antiseptic operation is not well understood: it is taken universally as a condiment to food, and it is employed in a number of chemical arts. The decomposition of it, so as to obtain its alkaline base, is a process of much importance, as affording a source whence soda can be abundantly procured. It has been attempted on the large scale by the intermedium of oxide of lead, of carbonate of potash, of lime and iron, and of sulphuric acid, the sulphate of soda being afterwards decomposed by the joint action of iron, lime, and charcoal; some of these processes are, from local circumstances, carried on with advantage.

MURIATE OF AMMONIA.—This is the sal-ammoniac of commerce, an important salt from the uses to which it is applied, and which is generally prepared on a large scale. The processes are various, but in general either the acid is directly combined with impure ammonia extracted from animal matter, or a sulphate of ammonia is procured, either by saturating this ammonia with sulphuric acid, or by maceration is extracted from soot, and is decomposed

by muriate of soda; the muriate of ammonia, formed by the operation of a double affinity, being sublimed. It is thus obtained in large semi-spherical cakes of a crystalline structure. By solution in boiling water and cooling it may be crystallized, its crystals being four-sided prisms. It is soluble in  $3\frac{1}{2}$  parts of water at  $60^{\circ}$ , and in its own weight of boiling water. It is volatilized by heat. It is used in soldering the metals, and in some of the processes of dyeing; and it is from this salt that ammonia is usually procured. In its formation equal volumes of the two gases combine, which, supposing the muriatic acid gas to contain 0.25 of water, gives the proportions of 33 of ammonia, 50.3 of acid, and 16.7 of water.

Muriate of barytes is soluble in three parts of cold water, and in a smaller quantity of hot water; it crystallizes from the latter solution on cooling in quadrangular tables. It is also soluble in alcohol; when freed from water it consists of 74 of barytes, and 26 of acid.—Muriate of Strontites is so soluble as to require no more than its weight of water at  $60^{\circ}$  to dissolve it: in boiling water it is still more soluble, and it crystallizes from this solution on cooling in slender six-sided prisms: its crystals are deliquescent.—Muriate of Lime is extremely soluble. By cooling its saturated solution, it may be obtained crystallized in six-sided prisms; these crystals are so deliquescent that they are not easily obtained dry; they liquefy on exposure to the air, and they combine rapidly with ice or snow, causing it to melt, and thus producing intense cold.—Muriate of Magnesia has such an affinity to water that it can be obtained in acicular crystals only by exposing its concentrated solution to sudden cold: these crystals are very deliquescent, and dissolve in less than their weight of water.—

Muriate of Argil can scarcely be crystallized, its solution becoming gelatinous on evaporation.—Muriate of Glucine is soluble in water, and, by evaporation, can be obtained in small crystals.—Muriate of Zircon is also soluble, and affords, by evaporation of its solution, transparent needle-like crystals.—Muriate of Ittria assumes a gelatinous form. On silix muriatic acid appears to exert some action, as, when this earth is newly precipitated, it is sensibly dissolved by the addition of the acid.

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A compound acid is formed by mixing muriatic acid and nitric acid, hence named NITRO-MURIATIC ACID, which has some peculiar properties, and which in particular dissolves gold with facility,—a property from which it received from the alchemists the name of Aqua Regia. One part of muriatic acid is mixed with two parts of nitric; during their combination the formation of oxymuriatic acid is indicated by its odour, nitric oxide gas is disengaged, and a portion of it is retained in the liquid, giving it a dark orange colour. It is concluded, therefore, that in the mutual action of these acids, part of the nitric acid is decomposed, its oxygen is transferred to the muriatic acid, and to the oxymuriatic acid thus formed the powers of the compound have been ascribed. It appears, however, to be chiefly a compound of nitric and muriatic acids, and its energetic action on the metals appears to be owing to the latter acid by a disposing or resulting affinity promoting the decomposition of the former, favouring therefore the communication from it of oxygen to the metal, with

which in its oxidated state it then combines. It is employed in some of the processes of assaying.

SECT. II.—*Of Oxymuriatic Acid.*

SCHÉELE discovered, that in the action of muriatic acid on black oxide of manganese, the acid suffers an entire change in its properties. A gas is disengaged of a greenish yellow colour, having an intolerable suffocating odour, not so easily condensed by water as muriatic acid gas, having much less acid power, and peculiarly distinguished by the property of destroying the vegetable colours. According to the views of chemical theory then adopted, he concluded, that this change is produced in muriatic acid by phlogiston being attracted from it by the black oxide of manganese. He therefore named it Dephlogisticated Muriatic Acid.

This theory, expressed according to the language of the more modern chemical system, implied merely, that the muriatic acid received oxygen. The new product, therefore, was named Oxymuriatic Acid, and this view of its constitution appeared to be confirmed by other facts. The oxide of manganese, on which it had acted, was found to be deprived of much of its oxygen: when the acid was submitted to the action of substances having an attraction to oxygen, as, for example, to the metals, these were found to be oxidated, while muriatic acid was at the same time reproduced. By the simple experiment even of exposing the solution of the oxymuriatic acid in water to the rays of the sun, very pure oxygen gas was found to be produ-



ced, accompanied with the transition to muriatic acid. Or, lastly, if the oxymuriatic acid were combined with alkaline bases, these compounds afforded a large quantity of pure oxygen when decomposed by heat, and in this case too muriatic acid was obtained. All these facts appeared to prove, that the gas formed by the action of muriatic acid on oxide of manganese; is a compound of that acid with oxygen, and, in conformity to this, it was further found, that it might be formed by the action of muriatic acid on other substances capable of affording oxygen.

The relation of muriatic acid to water, established by late experiments, leads to some modification of this opinion. In forming oxymuriatic gas, it appears, that the oxygen combines with the real muriatic acid; hence, when muriatic acid gas is employed in the experiment, its combined water is deposited; and, on the other hand, to admit of the decomposition of oxymuriatic acid, that portion of water must be supplied which is necessary to the constitution of the muriatic acid gas in its insulated form. The view of these phenomena, according to the hypothesis, that oxymuriatic acid is a simple substance, and muriatic acid a compound of it with hydrogen, has been already stated. It supposes that, in the experiment of the production of oxymuriatic gas, the oxygen imparted to the muriatic acid combines with its hydrogen and liberates the chlorine, and in the reproduction of muriatic acid hydrogen and chlorine again combine. The comparative merits of these doctrines have been already considered. The proportions of the elements of oxymuriatic acid have been variously stated, but from the quantity of oxygen obtained in its decomposition, and from the synthetic experiment of its production by the action of electricity on a mixture of muriatic acid

and oxygen, it appears to consist of about 28 of oxygen, and 77 of real acid. Oxymuriatic gas requiring an equal volume of hydrogen gas to convert it into muriatic acid gas, and hydrogen combining with half its volume of oxygen, it follows, that oxymuriatic gas contains half its volume of oxygen gas.

The process employed by Scheele to obtain oxymuriatic acid, consists in distilling with a moderate heat muriatic acid diluted with an equal weight of water from black oxide of manganese. It is more economical, and succeeds equally well to mix with the oxide, muriate of soda and sulphuric acid; four parts of muriate of soda being taken with one of black oxide, and three of sulphuric acid previously diluted with two of water. Their mutual action is favoured by a very gentle heat. The sulphuric acid combines with the soda of the muriate of soda, and disengages the muriatic acid, which, according to the common theory, receives oxygen from the black oxide of manganese; according to the other hypothesis, the oxygen of the oxide combines with the hydrogen of the muriatic acid, and forms water, while the other principle, the oxymuriatic gas, is merely set free.

The oxymuriatic acid is disengaged in the elastic form, and if it is to be submitted to examination under this form, may be received over warm water; quicksilver can scarcely be used as it is acted on. It may be condensed by passing it through cold water in the bottles of Woolfe's apparatus, and may thus be procured in a liquid state.

Oxymuriatic acid gas, though it retains its elasticity at low temperatures under a common atmospheric pressure, may be condensed by increased pressure; its specific gravi-

ty is 2.47; 100 cubic inches weigh 76.5 grains. It is the only gas that is visible, being discovered by its yellowish green colour; its odour is intolerably suffocating, and even when largely diluted with atmospheric air it produces an extreme sense of suffocation when it is respired.

It is absorbed by water in a quantity larger as the temperature is low; at  $50^{\circ}$  the water takes up about twice its volume. When the water is saturated with it, if it be cooled below  $40^{\circ}$ , it suffers a kind of congelation; soft scales are formed in it, and even crystals in the form of quadrangular prisms; these are the compound of the oxymuriatic acid and water: a moderate heat soon liquefies it. The solution has a yellowish green colour, and its odour is that of the acid itself; its taste is rather styptic than sour, and the liquid, like the gas, has the property of destroying the vegetable colours.

Liquid oxymuriatic acid is decomposed by exposure to light, pure oxygen gas being disengaged, and muriatic acid produced: In the gaseous state it suffers no change, as has been stated, the water necessary to its transition into muriatic acid being wanting. Neither does heat decompose the gas; but if it is transmitted through an ignited tube with watery vapour, oxygen gas and muriatic acid gas are obtained.

Oxymuriatic acid gas supports the combustion of a number of inflammable substances. A lighted taper burns in it though feebly; phosphorus takes fire when immersed in it, and a number of the metals, as antimony, arsenic, copper, or others, if introduced into it in leaves or filings, burn spontaneously. The alkaline metals burn vividly. This greater facility of supporting combustion is probably owing partly to the condensed state of the oxygen gas, and

partly to the disposing affinity of the muriatic acid promoting its action. The inflammable or metallic matter combines with the oxygen, and the oxidated product remains in union with the real acid. According to the hypothesis in which oxymuriatic gas is held to be a simple substance, it merely combines in these cases with the inflammable or metallic matter. In many of these combinations, different proportions are established with the same base. According to the common doctrine, these consist of the base in different degrees of oxidation combined with different proportions of muriatic acid; according to the new hypothesis, they consist of the base with different proportions of chlorine. Sir H. Davy distinguishes them by a peculiar nomenclature, the name of the compound being derived from that of the base, and the difference of proportion being indicated by a variation in the termination; the terminating syllable *ase* to denote the lower proportion, and *ana* to denote the higher, as mercurane, mercurana, cuprane, cuprana, &c. They are distinguished according to the other doctrine, merely as muriates in different degrees of oxidation.

Oxymuriatic gas and hydrogen inflame with detonation when the electric spark is taken in the mixture, and the introduction even of a wire heated to  $334^{\circ}$  inflames them; exposure to the rays of the sun has the same effect, and they act more slowly under diffused light. When they are in equal volumes, they are converted entirely into muriatic acid gas. The action on the carburetted hydrogen gases is similar; muriatic acid and carbonic acid are the products, with frequently a deposition of charcoal. Sulphuretted hydrogen is also decomposed, with inflammation if the gases are dry, and phosphuretted hydrogen is imme-

diately inflamed. The action of oxymuriatic gas on hydrogen is likewise shewn in its decomposing ammonia, the nitrogen of the decomposed ammonia remaining in the elastic form.

From the action of oxymuriatic gas on ammonia under peculiar circumstances, a very singular product, exceeding all others in detonating quality, is obtained. It was discovered by Dubong, a French chemist; and an extensive series of experiments has been made upon it by Messrs. Pörrat, Wilson and Kirk. To obtain it, a small jar is filled with pure oxymuriatic gas, and is transferred into a basin containing a solution of nitrate or muriate of ammonia a little warm; the gas is slowly condensed, and the liquor rises in the jar; an oily-like film forms on its surface, which increases and collects into globules, which at length fall through the liquor: this is the explosive compound. Its colour is yellowish; its specific gravity seems to be about 1.6; it evaporates speedily under exposure to the air, with a peculiar and very penetrating odour; in vacuo it assumes the elastic form at natural temperatures; it distils in close vessels at  $160^{\circ}$ , and does not freeze at  $-16^{\circ}$ ; it does not explode at  $200^{\circ}$ , but explodes violently at  $212^{\circ}$ : the most violent explosions, however, are produced from it when it is touched cold with inflammable bodies: a portion of it, for example, the size of a pin-head, being brought in contact with olive oil, the vessel is broken into fragments by the violence of the explosion; its effects are indeed so violent, as to have given rise to severe accidents; hence the propriety of the precaution of wearing a mask, and of taking care that the vessel in which it is formed, or the instrument by which it is removed, shall be perfectly clean and free from combustible matter. It is singular, that a number of

inflammable substances do not cause it to explode, such as charcoal, alcohol, or ether; and among the inflammable substances which either do, or do not cause it to explode, it does not appear that any analogy can be traced. Nitrogen gas is given out in these explosions; it gives the same gas from the action of muriatic acid, and with quicksilver it forms muriate of mercury, and affords nitrogen. Sir H. Davy, from some of these results, considered it as a compound of chlorine and nitrogen. From analytic experiments, Messrs Porret, Wilson and Kirk, conclude, that it consists of oxymuriatic acid, nitrogen and hydrogen: the hydrogen, they suppose, by its affinities to the other elements, serves as the medium of union; and the great explosive power of the compound they conceive owing to the action of oxymuriatic acid condensed in the combination, but at the same time retained only by a weak affinity. It is not improbable that it may be a hyper-oxymuriate of ammonia.

Charcoal freed from hydrogen by calcination does not burn in oxymuriatic acid gas, nor suffer any change; the cause of this has been already explained. The mixture of oxymuriatic gas with carbonic oxide gas cannot be inflamed by the electric spark. Messrs Gay-Lussac and Thenard stated, that neither do they act on each other under exposure to light, if they have been carefully freed from water, and I had obtained the same result. According to Mr J. Davy, they combine together and form a peculiar compound gas,—a difference of result which still requires investigation. This gas he names Phosgene, as being formed only under the influence of light. He describes it as having a penetrating odour different from that of chlorine, but still more intolerable; it reddens litmus paper, con-

denses four times its volume of ammoniacal gas, forming a neutral salt which is decomposed by liquid muriatic, nitric, sulphuric and phosphoric acids, affording carbonic and muriatic acid gases, but dissolves without effervescence in acetic acid. The gas is decomposed when heated with metals, carbonic oxide being obtained, and the products which the same metals form with chlorine. It is also decomposed by water, being converted into carbonic and muriatic acids. Mr J. Davy regards it as a compound of chlorine, and carbonic oxide, in equal volumes, condensed by their combination into half their volume, and from this condensation it must be the heaviest of the gases. According to the common theory, it would fall to be considered as a compound of real muriatic and carbonic acids.

Sulphur heated in oxymuriatic gas forms a liquid of a red colour, having a pungent odour, which smokes when exposed to the air, and is volatile. Dr Thomson obtained it by passing oxymuriatic gas over sulphur; regarding it as a compound of oxide of sulphur and muriatic acid, he named it Sulphuretted Muriatic Acid. It appears not to redden perfectly dry litmus paper; but when water is added, deposits sulphury, and affords sulphuric and muriatic acids.

Phosphorus inflames in oxymuriatic gas; a white solid condenses, which is very volatile, but may be fused under pressure, and then crystallizes: it reddens dry litmus paper, and combines with ammonia, forming a substance insoluble in water and perfectly fixed; by water it is resolved into muriatic and phosphoric acids. A compound somewhat analogous, containing more phosphorus, is obtained by heating muriate of mercury with phosphorus; it is a liquid, limpid, fuming and caustic; its vapour combining with humidity in the atmosphere is acid; when water is

added to it, it deposits phosphorous acid, and muriatic acid is disengaged.

One of the most important chemical properties of oxymuriatic acid is displayed in its action on the vegetable colours. Many of them it entirely destroys; and even those which are most deep and permanent, such as the colour of indigo, it renders faint, and changes to a light yellow or brown. This agency is exerted by it, both in its gaseous and its liquid form. The destruction of colour appears to be owing to the communication of oxygen to the colouring matter, for the oxymuriatic acid returns to the state of muriatic acid. The presence of water is necessary to this; hence, when the gas destroys colour, it must probably be enabled so to do by the hygrometric water it contains. It is accordingly affirmed, that when freed from this it does not destroy the colour of dry litmus paper.

Berthollet applied this agency of oxymuriatic acid to the process of bleaching, and with such success as to have entirely changed the manipulations of that art. The method of using it has been successfully improved. It consisted at first, in subjecting the thread or cloth to the action of the acid in the gaseous form, but the effect in this way was unequally produced, and the strength and texture were sometimes injured. It was then applied, condensed by water, and in a certain state of dilution. The thread or cloth is prepared as in the old method of bleaching, by boiling first in water, and then in an alkaline ley. It is then immersed in the diluted oxymuriatic acid: this alternate application of the acid and alkali being continued until the colour is discharged. The offensive suffocating odour of the acid rendered this mode of using it, however, scarcely practicable; the odour was found to be removed



by condensing the acid gas by a weak solution of potash : lime diffused in water being more economical, was afterwards substituted ; and more lately, slaked lime in the state of powder has been employed, the compound it forms with the acid being dissolved in water, so as to form the bleaching liquor of the proper strength. Under all these forms the oxymuriatic acid, by imparting oxygen to the colouring matter, weakens or discharges the colour, and the colouring matter appears to be rendered more soluble in the alkaline solution, alternately applied, and of course more easily extracted by its action. More lately, the improvement has been introduced of employing the potash alone, its solvent power being aided by applying it with the steam of water, at a high temperature under increased pressure ; and this has in part supplanted the use of the oxymuriatic acid. Mr Ramsay has substituted, with great advantage, oxymuriate of magnesia for that of lime, in whitening cloth for calico printing ; the cloth, when lime is used, retaining a little of it, which in the subsequent operation of clearing by immersion in weak sulphuric acid, forms sulphate of lime which affects the colours when it is dyed.

The relation of oxymuriatic acid to the alkalis and earths is peculiar. When presented to the alkali in a concentrated state, it undergoes decomposition ; a portion returns to the state of muriatic acid, and the other portion, with a quantity of oxygen, enters into combination with part of the alkaline base. It has been concluded from this, that no combinations of the oxymuriatic acid with the alkalis or earth exist. This appears, however, to be a mistake : when the acid and the alkaline solution are much diluted, their mutual action is rendered less energetic, and their direct combination is established : the proof of this is, that the

liquor thus formed retains the characteristic property of oxymuriatic acid, that of weakening or destroying the vegetable colours. These combinations, however, cannot easily be obtained in an insulated state, as there is no mode of concentrating their solution without giving rise to that re-action which produces decomposition. The compound formed by the introduction of oxymuriatic gas into the powder of hydrate of lime used in bleaching, is a mixture, according to Mr Dalton's analysis of it, of muriate and oxymuriate of lime.

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### SECT. III.—Of *Hyper-oxymuriatic Acid*.

WHEN a current of oxymuriatic acid gas is passed through an alkaline solution of a certain strength, a salt is deposited by spontaneous crystallization, which, by analysis, is found to contain a larger portion of oxygen, compared with the quantity of muriatic acid it contains, than it could do, supposing it to be a compound of oxymuriatic acid. A portion of the oxymuriatic acid returns also to the state of muriatic acid; a quantity of that acid, combined with a portion of the alkali, being found in the liquor. It has been concluded from these facts, in conformity to the established theory of the composition of oxymuriatic acid, that one portion of it yields oxygen to the other, one returns therefore to the state of muriatic acid, the other passes to the state of an acid containing more oxygen than the oxymuriatic acid, and each combines with a portion of the alkali present, so as to form neutral

compounds. The acid in the latter state has, in conformity to this view, been named Hyper-oxy muriatic Acid, and its salts are denominated Hyper-oxy muriates. Sir H. Davy has supposed, that this acid is a compound of chlorine and oxygen, and its salts ternary compounds of these two elements, and the base of the alkali of which they are formed.

• It was found difficult to obtain the hyper-oxy muriatic acid in an insulated form. When the hyper-oxy muriates are submitted to the action of sulphuric or nitric acid, with the view of disengaging it, the liquor around the salt becomes of an orange colour, and a small quantity of dense yellowish green vapour arises: if heat is applied to favour the action, an explosion is produced; or if this is avoided, the vapour disengaged has an intermixture of oxygen and oxy muriatic acid gases. Muriatic acid appeared to be converted into oxy muriatic acid by a similar process. Sir H. Davy found, however, that when the muriatic acid is in a certain state of dilution, it disengages a gas which appears to be the hyper-oxy muriatic acid. This process consists in adding to hyper-oxy muriate of potash in a retort, twice as much muriatic acid as will cover it, diluted with an equal volume of water. On applying heat, the gas comes over, and must be collected over mercury. He named it, from its bright yellow green colour, Euchlorine; and to his experiments we are indebted for a knowledge of its principal properties.

Its colour is a brighter yellow than that of chlorine, and its smell is different; its specific gravity is 2.410: 100 cubic inches weigh 74 or 75 grains; water absorbs 8 or 10 times its volume of it, and acquires its bright colour; it destroys vegetable colours, but first gives a tint of red. It

is remarkably distinguished by its facility of decomposition, and by this being accompanied with detonation and with light: a slight degree of heat, frequently even that of the hand, is sufficient to cause it to explode: in this explosion it is resolved into oxygen and oxymuriatic gases with enlargement of volume, 50 measures expanding to 60; of these, about 40 are oxymuriatic gas, and 20 oxygen gas: it seems to consist, therefore, of two measures of the former and one of the latter, condensed in the compound to half the volume of the oxygen gas. It is also decomposed by inflammables, and phosphorus kindled in it. None of the metals that burn in oxymuriatic gas burn in it at low temperatures; but if heat be applied, it is resolved into oxygen and oxymuriatic gas, and then from the action of the latter they take fire and burn.

It is not perfectly certain if the gas obtained by this process is exactly the acid which exists in the hyper-oxymuriates; there is no reason, however, to believe that they are materially different. These salts are peculiarly distinguished by the violent action they exert on inflammable bodies, producing with them deflagration or detonation by mere trituration: they afford very pure oxygen when decomposed by heat; they produce no precipitates with metallic salts, as the muriates do; neither do they retain the power of impairing the vegetable colours.

Of these salts the Hyper-oxymuriate of Potash is best known. To prepare it, a solution of four parts of sub-carbonate of potash in sixteen parts of water, from which the carbonic acid is abstracted by the action of lime, is put into the bottles of Woolfe's apparatus, and a current of oxymuriatic acid gas is passed through it, from a retort containing the materials from which this acid is disenga-

ged : this is continued until the alkali is neutralized : the hyper-oxy muriate of potash is deposited in scales, while a portion of muriate of potash remains in solution : one portion therefore of the oxymuriatic acid gas returning to the state of muriatic acid, has yielded its oxygen to the remaining portion, which has thus become hyper-oxy muriatic acid; and uniting with the alkali, forms hyper-oxy muriate of potash, these changes being probably owing to the strong affinity of the alkaline base to muriatic acid. According to the opposite hypothesis, the salt which has received this name is a ternary compound of oxymuriatic acid, oxygen, and potash or potassium.

Hyper-oxy muriate of potash crystallizes in scales, in needle-like crystals, or in thin quadrangular plates, white, and of a silvery lustre. It is soluble in 17 parts of water at 60°, and in two parts and a half at 212; it melts from the application of a moderate heat: when heated to redness it is decomposed, and very pure oxygen gas is expelled. Chenevix found, that 100 grains freed from water yield 38.3 of oxygen, and the residue contained 20 of muriatic acid; it consists therefore of 58.3 of oxymuriatic acid, 39.2 of potash, and 2.5 of water of crystallization.

Hyper-oxy muriate of potash is decomposed by the acids. Thrown into sulphuric acid it decrepitates, the liquor acquires an orange colour, and a dense yellowish green vapour is disengaged. If heat is applied, an explosion with a vivid flash of light takes place; if the acid be diluted so as to admit of the application of heat with safety, the elastic fluid which is disengaged is a mixture of oxymuriatic acid and oxygen. The action of nitric acid is similar, but less violent: Muriatic acid is converted into oxymuriatic acid. The elastic fluid disengaged in

these decompositions acts with considerable force on inflammable substances ; two or three grains of the salt, for example, mixed with half the quantity of sulphur, charcoal, resins, or oils, forming mixtures which are kindled by the contact of sulphuric or nitric acid.

The salt itself acts with still more energy on inflammable bodies. If a grain or two be triturated with half its weight of sulphur or charcoal, or if the mixture in these proportions be struck forcibly, a loud detonation is produced. A similar effect is produced when several of the metals are employed ; and with phosphorus the detonation is so violent, that it can be made with safety only on a very small quantity. These mixtures are also inflamed by the electric discharge and by applying heat. These effects appear to arise from the rapid combination of the oxygen of the salt with the inflammable body, and the formation in general of an elastic product : experiment ought to be made only on small quantities of the materials.

The other hyper-oxy muriates scarcely require particular notice. The hyper-oxy muriate of soda is not so easily obtained pure as that of potash, as it is nearly of the same degree of solubility with muriate of soda, and is therefore not easily separated from it by crystallization. It crystallizes in cubes, is deliquescent, and is soluble in three parts of cold water. Hyper-oxy muriate of ammonia is formed by decomposing carbonate of ammonia by hyper-oxy muriate of lime ; is very soluble in water and in alcohol, and is decomposed by a slight elevation of temperature. Hyper-oxy muriate of barytes is soluble and crystallizable, as is also that of strontites ; hyper-oxy muriate of lime is deliquescent, and soluble in water and alcohol ; hyper-oxy muriate of magnesia has nearly the same properties.

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## CHAP. VII.

### OF FLUORIC ACID, ITS BASE, AND COMBINATIONS.

THIS acid was discovered by Scheele as a constituent principle of the mineral known by the name of Fluor Spar, in which it is combined with lime: It has since been discovered in a few other minerals; and also in the animal kingdom, particularly in the enamel of the teeth, and in the fossil or petrified teeth of the elephant. Some important discoveries with regard to it have lately been made by Gay-Lussac and Thenard, the pure acid having been obtained by them, and having qualities altogether different from those belonging to what had been considered as fluoric acid.

The usual process for procuring fluoric acid consisted in submitting fluor spar in coarse powder to the action of twice its weight of sulphuric acid, using a leaden retort, on account of a singular property of this acid, that it dissolves siliceous earth, and hence acts on glass. The sulphuric acid combines with the lime of the fluor spar, and the fluoric acid assumes the gaseous form. The gas may be collected over mercury, as it is absorbed by water; or if it is to be condensed, the retort is connected with a leaden receiver, containing a sufficient quantity of water. In this way, however, it has always a contamination of silic, either from the fluor spar, which often contains this earth, or from the glass receiver. The process given by

Gay-Lussac and Thenard is, to select very pure fluor spar, and decompose it, by applying heat to a mixture of it with sulphuric acid in a leaden retort, connected with a leaden receiver, which is kept cool with ice. The fluoric acid is condensed in the liquid form, and does not exist in the gaseous state, as had been before believed.

It retains this liquid form even at  $60^{\circ}$  of Fahrenheit, but boils at a heat not much higher; it must be excluded from the air, as otherwise it evaporates speedily; and it must be preserved in metallic vessels, those of silver or lead, as it immediately assumes the gaseous form on coming into contact with glass, from dissolving a portion of its silex. It forms white vapours in the atmosphere, by combining with its humidity; its odour is very penetrating; and one of its most remarkable properties is its extreme causticity, in consequence of which it instantly destroys the skin, when the smallest drop touches it, exciting severe pain, causing suppuration, and by the great irritation to which it gives rise affecting even the general system: much caution, therefore, is necessary in making experiments with it. It combines with water with rapidity, producing a hissing noise and much heat.

The saline compounds of this acid have the name of Fluates. Their properties were unknown in their pure state, previous to the experiments of the French chemists. Fluato of potash has a sharp taste, is deliquescent, very soluble in water, and not easily crystallizable. Fluato of soda is less sapid, is neither deliquescent nor efflorescent; is more soluble in hot than in cold water, and its solution on cooling affords minute crystals. Fluato of ammonia has a very sharp taste, is volatile and easily decomposed. The fluates of barytes, strontites, lime, magnesia and argil are insolu-



ble, but become soluble from an excess of acid. Fluates of lime is obtained in nature in a very different state, forming fluor-spar, often crystallized in large and regular cubes, transparent, of rich colours, vitreous lustre, hard and brittle.

The relation of this acid to siliceous earth forms a very striking character of it, as it is the only one which dissolves silex in considerable quantity. It acts on it rapidly, and at the same time assumes the gaseous state, forming what used to be regarded as fluoric acid, but what may be named Siliceo-fluoric acid. This is usually obtained by adding sulphuric acid to a mixture of pounded fluor-spar and flint: the fluoric acid disengaged, saturates itself with the silex of the flint, and forms a permanent gas. This is one of the heaviest of the gases, its specific gravity being 2.990; 100 cubic inches weigh 91 grains: it has a pungent odour, is corrosive and acid: it forms white vapours when diffused in the atmosphere, by attracting hygrometric water and condensing. It is largely absorbed by water, and at the same time deposits a considerable part of the silex which it holds dissolved in a kind of gelatinous deposite, the acid with the remaining silex forming a soluble compound. According to Mr J. Davy, the acid gas consists of 88.6 of fluoric acid, and 61.4 of silex; in the liquid acid 54.56 of silex are combined with 45.44 of acid. It does not appear to produce the state of neutralization; though from the liquid solution crystals have been said to be deposited after a length of time, which some have regarded as fluates of silex.

From the strong affinity of this acid to siliceous earth, it retains a portion of it when it unites with salifiable bases, forming ternary compounds. These were formerly regard-

ed as pure fluates: they may be named *Siliceo-fluates*. Their properties are not very important; and they do not indeed differ much from the compounds of the pure acid with the same bases. The siliceo-fluoric acid gas condenses, as Gay-Lussac has remarked, twice its volume of ammoniacal gas.

From its strong action on *silex*, fluoric acid has been employed to engrave on glass.

The action of this acid on the metals does not seem to be very energetic; but it combines with their oxides, forming in general insoluble compounds.

The composition of fluoric acid has not been ascertained, but it has some peculiarities of chemical constitution, similar to muriatic acid. When potassium is introduced into the pure liquid acid, it produces the most rapid inflammation and even detonation, hydrogen gas is disengaged, and a liquid is obtained, which is a solution of super-fluate of potash. It appears from this, therefore, that the acid in this state contains combined water, which is decomposed by the potassium, and the real acid remains combined with the potash formed. It also appears, that the acid cannot be obtained insulated free from water, for it cannot be disengaged pure from its combinations, but by an acid which affords water. But it exists in this state not only in its saline compounds, but in others in which it is scarcely neutralized. Thus, it appears to be free or nearly so from combined water in the siliceo-fluoric acid gas, and it is also in this state in another singular compound which it forms with boracic acid. In all these respects, the analogy to muriatic acid is sufficiently obvious. An opposite view may therefore be given of these facts, on similar grounds,—that it does not contain water, but consists of hydrogen

united with an unknown principle. This conjecture has been advanced by Sir H. Davy, who has given this unknown substance the name of Fluorine. In siliceo-fluoric acid, he supposes it to be combined with the metallic base of *silex*, and in fluo-boric acid with boron.

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Gay-Lussac and Thenard, in endeavouring to procure fluoric acid free from combined water, had submitted to heat a mixture of two parts of fluor-spar with one part of dry boracic acid in a coated iron tube. An elastic fluid was collected over quicksilver, without colour, having a penetrating odour, and powerfully acid so as to redden the vegetable colours. Finding it to be a compound of fluoric and boracic acids, they named it Fluo-boric acid.

A distinguishing character of this substance is the strength of its attraction to watery vapour, and its forming with it very dense vapours: hence it is the most delicate test of the presence of hygrometric vapour in any other elastic fluid. It is absorbed by water in a quantity as large as muriatic acid gas is, and with great rapidity; and when the water is saturated, a very dense acid, resembling sulphuric acid in appearance, is formed: this is highly corrosive, and it acts on animal and vegetable substances like sulphuric acid, charring them, and causing a formation of water. It does not, however, affect the skin like pure fluoric acid; nor does it act on siliceous earth. It exhales vapours when exposed to the air, and distils at a high degree of heat.

Fluo-boric acid combines with the alkalis and earths. The salt it forms with ammonia is decomposed by heat, fluato of ammonia with a portion of borate of ammonia is sublimed, and concrete boracic acid remains. By this analytic experiment, Gay-Lussac and Thenard demonstrated the constitution of fluo-boric acid. It appears not to contain that portion of combined water peculiar to both of these acids in their insulated form. When acted on by potassium, boron is obtained with fluato of potash.

## TABLE OF AFFINITIES.

| I.<br>OXYGEN. | IV.<br>CARBON. | VII.<br>AMMONIA, POTASH AND SODA. | Muriatic    | Succinic      |
|---------------|----------------|-----------------------------------|-------------|---------------|
| Carbon        | Oxygen.        | Acids                             | Citric      | Phosphoric    |
| Zinc          | Iron           | Sulphuric                         | Tartaric    | Saccho-lactic |
| Iron          | Hydrogen       | Nitric                            | Arsenic     | Nitric        |
| Hydrogen      | V.             | Muriatic                          | Benzoic     | Muriatic      |
| Manganese     | SULPHUR.       | Fluoric                           | Acetic      | Fluoric       |
| Cobalt        | —              | Phosphoric                        | Boracic     | Arsenic       |
| Nickel        | Oxygen         | Oxalic                            | Sulphurous  | Citric        |
| Lead          | Potash         | Tartaric                          | Nitrous     | Benzoic       |
| Tin           | Soda           | Arsenic                           | Carbonic    | Acetic        |
| Phosphorus    | Iron           | Succinic                          | Prussic     | Boracic       |
| Copper        | Copper         | Citric                            | Sulphur     | Sulphurous    |
| Bismuth       | Tin            | Benzoic                           | IX.         | Nitrous       |
| Antimony      | Lead           | Acetic                            | STRONTITES. | Carbonic      |
| Quicksilver   | Silver         | Saccho-lactic                     | —           | Prussic       |
| Arsenic       | Bismuth        | Boracic                           | Acids       | Sulphur       |
| Sulphur       | Antimony       | Sulphurous                        | Sulphuric   | XI.           |
| Gold          | Quicksilver    | Nitrous                           | Oxalic      | MAGNESIA.     |
| Silver        | Arsenic        | Carbonic                          | Tartaric    | Acids         |
| Platina       | Molybdena      | Prussic                           | Fluoric     | Oxalic        |
| Muriatic Acid | Tellurium      | Water                             | Nitric      | Phosphoric    |
| II.           | VI.            | Oil                               | Muriatic    | Sulphuric     |
| NITROGEN.     | SULPHURETTED   | Sulphur                           | Succinic    | Fluoric       |
| Oxygen        | HYDROGEN.      | VIII.                             | Phosphoric  | Arsenic       |
| Hydrogen      | —              | BARYTES.                          | Acetic      | Saccho-lactic |
| III.          | Barytes        | —                                 | Arsenic     | Succinic      |
| HYDROGEN.     | Potash         | Acids                             | Boracic     | Nitric        |
| Oxygen        | Soda           | Sulphuric                         | Carbonic    | Muriatic      |
| Sulphur       | Lime           | Oxalic                            | Sulphur     | Tartaric      |
| Carbon        | Ammonia        | Succinic                          | X.          | Citric        |
| Phosphorus    | Magnesia       | Fluoric                           | LIME.       | Benzoic       |
| Nitrogen      | Zircon         | Phosphoric                        | —           | Acetic        |
|               |                | Saccho-lactic                     | Acids       | Boracic       |
|               |                | Nitric                            | Oxalic      | Sulphurous    |
|               |                |                                   | Sulphuric   | Carbonic      |
|               |                |                                   | Tartaric    | Prussic       |
|               |                |                                   |             | Sulphur       |

| XII.<br>ARGIL. | Potash<br>Soda<br>Lime<br>Magnesia<br>Ammonia<br>Argil<br>Metallic Oxides                          | Argil<br>Metallic Oxides   | Potash<br>Soda<br>Ammonia<br>Argil<br>Metallic Oxides            | Magnesia<br>Argil<br>Metallic Oxides   |
|----------------|--|--|--|--|
| Acids          |  | XX.<br>FLUORIC ACID.   | XXVI.<br>BENZOSC ACID.   | XXXI.<br>ALCOHOL.  |
| Sulphuric      |  | The same as in<br>NO. 18.  | The same as in<br>NO. 25.  | Water<br>Ether   |
| Nitric         | XVII.<br>SULPHUROUS<br>ACID.   | XXI.<br>BORACIC ACID.  | XXVII.<br>SUCCINIC ACID.   | Volatile Oils<br>Ammonia   |
| Muriatic       | Barytes<br>Strontites  | The same as in<br>NO. 18.  | The same as in<br>NO. 25.  | Fixed Alkalies<br>Sulphur<br>Muricates   |
| Fluoric        | Lime   | XXII.<br>ARSENIC ACID.   | XXVIII.<br>LACTO-LACTIC<br>ACID.                                 | XXXII.<br>ETHER.   |
| Oxalic         | Potash<br>Soda   | Lime<br>Barytes<br>Strontites<br>Magnesia<br>Potash<br>Soda<br>Ammonia<br>Argil<br>Metallic Oxides | The same as in<br>NO. 25.  | Alkohol<br>Volatile Oils<br>Water  |
| Tartaric       | Magnesia<br>Ammonia<br>Argil<br>Metallic Oxides  | XXIII.<br>OXALIC ACID.   | XXIX.<br>ACETIC ACID.  | XXXIII.<br>VOLATILE OILS.  |
| Phosphoric     | XVIII.<br>PHOSPHORIC<br>ACID.  | The same as in<br>NO. 18.  | Barytes<br>Potash<br>Soda<br>Ammonia<br>Argil<br>Metallic Oxides | Ether<br>Alkohol<br>Fixed Oil<br>Fixed Alkalies<br>Sulphur                                     |
| Acetic         | Lime<br>Barytes<br>Strontites<br>Magnesia<br>Potash<br>Soda<br>Ammonia<br>Argil<br>Metallic Oxides | XXIV.<br>TARTARIC ACID.  | XXX.<br>PRUSSIC ACID.  | XXXIV.<br>FIXED OILS.  |
|                | XIX.<br>CARBONIC<br>ACID.  | The same as in<br>NO. 18.  | Potash<br>Soda<br>Ammonia<br>Lime<br>Barytes<br>Strontites       | Lime<br>Metallic Oxides<br>Ether<br>Volatile Oil<br>Fixed Alkali<br>Volatile Alkali<br>Sulphur |
|                | Barytes<br>Strontites<br>Lime<br>Fixed Alkalies<br>Magnesia<br>Ammonia                             | XXV.<br>CITRIC ACID.   |  |  |

TABLE OF THE CAPACITIES OF A NUMBER OF BODIES FOR CALORIC, BY CRAWFORD, AND IRVINE.

*Gases.*

|                         |            |
|-------------------------|------------|
| Hydrogen gas,.....      | 21.4000 C. |
| Oxygen gas,.....        | 4.7490 —   |
| Atmospheric air,.....   | 1.7900 —   |
| Aqueous vapour,.....    | 1.5500 —   |
| Carbonic acid gas,..... | 1.0454 —   |
| Nitrogen gas,.....      | .7936 —    |

*Liquids.*

|                         |          |
|-------------------------|----------|
| Arterial blood,.....    | 1.0360 — |
| Water,.....             | 1.0000 — |
| Milk,.....              | .9899 —  |
| Alkohol,.....           | .8500 I. |
| Venous blood,.....      | .8928 C. |
| Alkohol,.....           | .6081 —  |
| Spermaceti oil,.....    | .5000 —  |
| Sulphuric acid,.....    | .4290 —  |
| Oil of turpentine,..... | .4000 —  |
| Sulphuric acid,.....    | .3380 —  |

*Solids.*

|                                      |          |
|--------------------------------------|----------|
| Ice,.....                            | .8000 I. |
| Flesh,.....                          | .7400 C. |
| Rice,.....                           | .5060 —  |
| Barley,.....                         | .4210 —  |
| Pit-coal,.....                       | .2777 —  |
| Charcoal,.....                       | .2631 —  |
| Chalk,.....                          | .2564 —  |
| White oxide of antimony washed,..... | .2272 —  |
| Oxide of copper,.....                | .2272 —  |
| Quicklime,.....                      | .2229 —  |
| Oxide of iron,.....                  | .1666 —  |
| Glass,.....                          | .2000 I. |
| Iron,.....                           | .1430 —  |
| Oxide of antimony,.....              | .1666 C. |
| Oxide of zinc,.....                  | .1369 —  |
| Iron,.....                           | .1269 —  |

|                            |          |
|----------------------------|----------|
| Brass,.....                | .1123 C. |
| Copper,.....               | .1111 —  |
| White oxide of tin,.....   | .0990 —  |
| Zinc,.....                 | .0943 —  |
| Tin,.....                  | .0704 —  |
| Yellow oxide of lead,..... | .0680 —  |
| Antimony,.....             | .0645 —  |
| Lead.....                  | .0352 —  |

TABLE OF THE CAPACITIES OF THE GASES FOR CALORIC BY  
BERARD.

|                      |         |
|----------------------|---------|
| Water,.....          | 1.0000  |
| Air,.....            | .00009  |
| Hydrogen,.....       | .000006 |
| Carbonic acid,.....  | .000010 |
| Oxygen,.....         | .000011 |
| Nitrogen,.....       | .000014 |
| Nitrous oxide,.....  | .000019 |
| Oleasant gas,.....   | .000027 |
| Carbonic oxide,..... | .000034 |
| Watery vapour,.....  | .000070 |

TABLE OF THE SCALE OF TEMPERATURE, AND OF THE MELTING  
AND BOILING POINTS OF A NUMBER OF BODIES.

|   | Wedge. | Fahren. |
|---|--------|---------|
| Extremity of the scale of Wedgwood's pyrometer.....   | 240°   | 392.77° |
| Greatest heat of an air furnace, which neither melted nor<br>softened Nankkeen porcelain..... | 160    | 218.77  |
| Chinese porcelain softened.....   | 156    | 213.57  |
| Cast iron melted.....   | 150    | 205.77  |
| Greatest heat of a smith's forge.....   | 125    | 173.37  |
| Greatest heat of a glass furnace.....   | 114    | 158.97  |
| Welding heat of iron.....   | 95     | 132.77  |
| Gold melts.....   | 32     | 52.37   |
| Silver melts.....   | 28     | 47.17   |
| Copper melts.....   | 27     | 45.87   |
| Brass melts.....  | 21     | 38.07   |
| Red-heat visible in day light.....  | 0      | 10.77   |



|  | Fahren. |
|--|---------|
| Red-heat in twilight.....  | 884½    |
| Heat of a common fire.....   | 790     |
| Iron bright red in the dark.....                                       | 752     |
| Zinc melts.....  | 700     |
| Quicksilver boils.....   | 672     |
| Linseed oil boils.....   | 600     |
| Lead melts.....  | 594     |
| Sulphuric acid boils.....  | 590     |
| Sulphur burns.....   | 590     |
| Phosphorus boils.....  | 554     |
| Bismuth melts.....   | 476     |
| Tin melts.....   | 442     |
| Nitric acid boils.....   | 242     |
| Sulphur melts.....   | 226     |
| Water boils (the barometer being at 30 inches).....                    | 212     |
| Alkohol boils.....   | 174     |
| Phosphorus melts.....  | 100     |
| Ether boils.....   | 98      |
| Heat of the human blood.....   | 98      |
| Medium temperature of the globe.....                                   | 50      |
| Ice melts.....   | 32      |
| Strong wines freeze at about.....                                      | 20      |
| Melting point of quicksilver.....                                      | 39      |
| Liquid ammonia crystallizes.....                                       | 42      |
| Nitric acid, spec. gr. about 1.42, freezes.....                        | 45      |
| Sulphuric ether congeals.....  | 47      |
| Natural temperature observed at Hudson's Bay.....                      | 50      |
| Ammoniacal gas condenses into a liquid.....                            | 54      |
| Cold from diluted sulphuric acid and snow, the materials being at..... | 57 — 78 |
| Greatest cold yet measured.....  | 91      |

TABLE OF FREEZING MIXTURES.

|  | Temperature reduced. |
|--|----------------------|
| Muriate of ammonia, 5 parts, nitrate of potash 5, water 16,                            | from 50° to 10°      |
| Muriate of ammonia, 5 parts, nitrate of potash 5, sulphate }<br>of soda 8, water 16,   | 50 to 4              |
| Nitrate of ammonia 1, water 1,   | 50 to 4              |
| Sulphate of soda 8, muriatic acid 5,   | 50 to 0              |
| Sulphate of soda 5, sulphuric acid diluted with an equal }<br>weight of water 4 parts, | 50 to 5              |
| Sulphate of soda 6, muriate of ammonia 4, nitre 2, diluted }<br>nitric acid 4,         | 50 to -10            |
| Phosphate of soda 9, diluted nitric acid 4,  | 50 to -12            |
| Muriate of soda 1, snow 2 parts,   | 32 to -6             |
| Nitric acid diluted, snow,   | 32 to -10            |
| Concentrated sulphuric acid, snow,   | 32 to -10½           |
| Muriate of soda 2, muriate of ammonia 1, snow 5,                                       | 32 to -12            |
| Carbonate of potash, snow,   | 32 to -17            |
| Muriate of soda 10, nitrate of potash 5, snow 24,                                      | 32 to -18            |
| Sulphuric acid diluted with one-half its weight of water, }<br>2 parts, snow 3 parts,  | 32 to -22            |
| Concentrated muriatic acid 5, snow 8,  | 32 to -27            |
| Concentrated nitrous acid 4, snow 7,   | 32 to -30            |
| Muriate of lime 5, snow 4,   | 32 to -40            |
| ————— 3, ——— 2,  | 32 to -50            |
| ————— 5, ——— 3,  | 32 to -53            |
| Potash 4, snow 3,  | 32 to -51            |
| Muriate of lime 2, snow 1,   | 0 to -66             |
| ————— 3, snow 1,   | -40 to -73           |
| Sulphuric acid with half its weight water 10, snow 8,                                  | -68 to -91           |

TABLE OF THE PROPORTIONS OF DIFFERENT COMPOUNDS WHOSE ELEMENTS ARE GASEOUS, BY GAY-LUSSAC.

| Substances.                  | Proportions in volume. |                   | Proportions in weight. |                 |
|------------------------------|------------------------|-------------------|------------------------|-----------------|
| Muriate of ammonia           | 100 gas am.            | 100 gas mur. am.  | 38,35                  | ac. mur. 61,65  |
| Carbonate of ammonia neutral | 100 idem               | 100 g. carb. idem | 28,19                  | ac. carb. 71,81 |
| Sub-car. of ammonia          | 100 idem               | 50 idem           | idem 43,98             | idem 56,02      |
| Fluo-borate of ammonia       | 100 idem               | 100 g. fluob.     |                        |                 |
| Sub-fluo-borate of ammonia   | 100 idem               | 50 idem           |                        |                 |
| Water                        | 100 gas hyd.           | 50 gas oxy.       | oxy. 86,733            | hyd. 13,267     |
| Nitrous oxide gas            | 100 nitrog.            | 50 oxygen         | nitrog. 63,72          | oxy. 36,28      |
| Nitric oxide gas             | 100 idem               | 100 idem          | idem 46,757            | idem 53,243     |
| Nitric acid                  | 100 idem               | 200 idem          | idem 30,512            | idem 69,488     |
| Nitric acid                  | 200 g. nit.            | 100 gas oxy.      | idem                   | idem            |
| Nitrous acid gas             | 300 idem               | 100 idem          | nitrog. 54,507         | idem 65,493     |
| Ammonia                      | 100 nitrog.            | 300 hydr.         | idem 81,525            | hyd. 18,475     |
| Sulphuric acid.              | 100 sulphurous acid    | 50 gas oxy.       | sulph. 42,016          | oxy. 57,984     |
| Sulphurous acid              |                        |                   | idem 52,083            | idem 47,91      |
| Oxymuriatic acid             | 300 g. mur.            | 100 oxygen        | A. mur. 77,65          | oxy. 22,35      |
| 100 Carbonic acid gas        | 100 g. oxide of carbon | 50 gas oxy.       | carb. 27,376           | oxy. 72,624     |
| 100 Carbonic acid gas        |                        | 100 oxygen        | idem                   | idem            |
| 100 Carbonic oxide           | 50 gas oxyg.           |                   | carb. 42,99            | oxy. 57,10      |

TABLE OF THE PROPORTIONS OF THE CONSTITUENT PRINCIPLES OF COMPOUND GASES, BY DALTON.

| Names of the compounds. | Constituent principles of 100 measures of the compound. |             | Constituent principles of 100 weight of the compound. |            |
|-------------------------|---|-------------|---|------------|
|                         | M. mesures.   | M. mesures. |   |            |
| Ammon. gas              | 52 azote  | 153 hyd.    | 83 azote  | 17 hyd.    |
| Water                   | 100 oxyg.   | 200 hyd.    | 87 oxy.   | 12.5 hyd.  |
| Nitrous gas             | 46 azote  | 55 oxyg.    | 42 azote  | 58 oxygen  |
| Nit. oxide              | 99 azote  | 58 oxyg.    | 59 azote  | 41 oxygen  |
| Nitric acid             | 180 nit. gas  | 100 oxy.    | 27 azote  | 73 oxygen  |
| Nitrous acid            | 360 nit. gas  | 100 oxy.    | 43 azote  | 67 oxygen  |
| Oxym. acid              | 150 mur. acid   | 50 oxy.     | 76 mur. acid  | 24 oxygen  |
| Sulphs. acid            | 100 oxygen  | sulphur     | 52 oxy.   | 48 sulphur |
| Sulphc. acid            | 100 sul. acid   | 5 oxy.      | 79; sul. acid   | 20½ oxyg.  |
| Carb. oxide             | 47 oxy.   | charcoal    | 55 oxy.   | 45 charc.  |
| Carb. acid              | 100 oxy.  | charcoal    | 72 oxy.   | 28 charc.  |
| Carbur. hyd.            | 200 hydr.   | 1 part ch.  | 27 hyd.   | 73 charc.  |
| Olefant gas             | 200 hydr.   | 2 parts ch. | 15 hyd.   | 85 charc.  |
| Sulph. hyd.             | 100 hydr.   | sulphur     | 7 hyd.  | 93 sulph.  |
| Mur. of am.             | 100 mur. acid   | 100 am. g.  | 65 mur. acid  | 35 am. gas |
| Carb. of am.            | 100 carb. acid  | 80 am. g.   | 76 carb. acid   | 24 am. gas |
| Subc. of am.            | 100 carb. acid  | 160 am. g.  | 61 carb. acid   | 39 am. gas |